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# THEORIES OF CRYSTALLIZATION

BY  
SVAANTE ARRHENIUS

EDITED BY  
J. CLAYTON FRIGGE



# THEORIES OF CHEMISTRY

*BY THE SAME AUTHOR*

A TEXT-BOOK OF  
**ELECTRO-CHEMISTRY**

TRANSLATED FROM THE  
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JOHN McCRAE, PH.D.

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# THEORIES OF CHEMISTRY

BEING

*LECTURES DELIVERED AT THE  
UNIVERSITY OF CALIFORNIA, IN BERKELEY*

BY

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GENERAL  
INFO

## P R E F A C E

THE present lectures were delivered at the University of California, in Berkeley, during the summer of 1904.

I have for a long time wished to give a coherent account of the development of theories in general chemistry. This seemed to me the more desirable because the latest extensions of this science are often, both by its followers and by its opponents, regarded as something wholly new and quite independent of the progress in the past.

Many seem to hold the opinion that the new developments are the more to be admired, the less dependent they are on the older chemical theories. In my opinion, nothing could be less correct. It is just the circumstance that the new theoretical discoveries have developed organically from the old generally accepted ideas, that is to me their most promising feature. I hope to make clear in these lectures that the new chapters in theoretical chemistry are a consequent and necessary continuation of the old science, according to the method which has ruled the development of chemistry as an exact branch of knowledge in the last century. If the scientists, who believe that it is possible to undermine the more modern parts of this scientific edifice, had thoroughly considered the matter, they would find that their efforts, if successful, would simultaneously demolish the neighbouring older parts, which, however, they consider to be so firmly established that they cannot be overthrown even by the most vigorous attacks. These opponents would, therefore, be better advised to confine themselves to the replacement of some of the building-stones by new ones, or to

the elaboration of some of the external features, or perhaps, also, to the strengthening of the foundations. But they should not necessarily try to alter the style of the newly built parts, for this style is a consequence of the modern method of working and of the nature of the scientific material of the building. The working method, as well as the materials, is, on the whole, of nearly the same kind now as when Boyle, Lavoisier, Richter, and Dalton laid the foundations of modern chemistry.

If we consider the historical development of our science, we find that very often—in fact, nearly always—the new builders, when they carried out their work, did not know, or at least did not take into consideration, the plans of the older parts. Nevertheless, we observe that similar styles have been used both now and in the past. This fact is due to the circumstance that we have learnt to work by the aid of the experience collected during generations. It is scarcely of use to examine whether the construction would have proceeded more rapidly if the scientists of to-day had always kept the building plans of the old masters in view. I can only express my personal opinion, which is, that the present mode of working is the most fruitful one. In reality, the working method changes slowly as better working instruments are introduced, and at the same time, without ourselves observing it, we also modernize the older parts of the building, bringing them into perfect agreement with the newer ones, by many small alterations which are hardly noticeable.

It is the extreme ease with which this adaptation of the older parts to the newer ones can be effected that gives the best proof of the soundness and validity of our theoretical ideas. I venture to hope that all who read these lectures will find that the recent developments in theoretical chemistry can be submitted to this test with confidence.

To the lectures held in Berkeley I have added some remarks in reference to recent publications bearing on theoretical questions. I am indebted to my friends Prof. W. Tate (of Calcutta)

and Dr. T. Slater Price for revision of the manuscript, and for many friendly hints and criticisms. By the publication of these lectures I also wish to recall many pleasant memories to my Californian friends and colleagues, who gave me such a cordial and unforgettable reception in their beautiful country.

**THE AUTHOR.**

STOCKHOLM,

*February, 1907.*



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# THEORIES OF CHEMISTRY

## CHAPTER I

### *INTRODUCTION: THE USE OF THEORIES*

IN the following lectures I shall have the honour of bringing before you some account of the development of theories in chemistry.

To commence, then, at the beginning, we have to ask ourselves: "What is the characteristic feature of a theory?" Most people would answer: "A theory is something unpractical." Nothing could be more incorrect. It is just the contrary. As Boltzmann once said, "A theory should be the most practical exposition of facts." As an example he cites the theory of the conduction of electricity, the greater part of which is embodied in Ohm's law. Before Ohm had formulated his law, which he deduced from theoretical considerations, an endless number of experiments were made to ascertain the connection between the strength of a current (estimated either according to the brightness of the sparks produced on breaking the circuit, or from the deflection of a magnet) and the number of voltaic cells used for its production. The cells, however, did not possess a constant resistance, and their electromotive force changed rapidly with the time, so that it was very difficult to deduce the law, expressing the connection sought for, from purely experimental data.

Ohm,<sup>1</sup> however, applied deductions which he derived mainly from the results of Fourier's classical researches on the conduction of heat. Just as the quantity of heat flowing through

<sup>1</sup> Cf. Ohm, *Die galvanische Kette*, Neudruck. Leipzig and Wien: Toeplitz and Deuticke. 1887.

a parallelopiped, the ends of which are maintained at the constant temperatures  $t_1$  and  $t_0$  respectively, is proportional to the cross-section and inversely proportional to the length of the parallelopiped, also proportional to the difference of temperature ( $t_1 - t_0$ ) and to a constant, called the specific conductivity for heat, characteristic of the substance of which the parallelopiped is made; so, in the same way, the current of electricity through a parallelopiped (*e.g.* a cylinder or a wire) ought to be proportional to the cross-section and inversely proportional to the length of the parallelopiped, also proportional to the difference of electrical potential between its end surfaces and to a constant, called the specific electrical conductivity, characteristic of the substance. In this way Ohm arrived at his law, and all experiments which have since been made on the strength of electric currents have verified it.

Now, even if Ohm's law had only been true for weak currents, and deviations from it had been found for strong currents, it would nevertheless have been extremely useful. Because of its *quantitative* formulation, it was possible to calculate the strength of a given current and compare this calculated value with the observed one. If now both had not agreed within the limits of experimental error, it would have been necessary to seek for the cause of this deviation. In this way we should have found either that the electromotive force (*i.e.* the potential difference) applied to the ends of the wire was not that used in the calculation, or that a wrong value had been assumed for the constant representing the electrical conductivity of the wire. We should then have made a new experiment, taking care that the electromotive force and the conductivity were of the supposed values, and then observed if the value of the current agreed with that of the previous observation or with the calculated value, within the limits of experimental error. In the latter case an experimental proof of the truth of the law would have been given. This proof has been obtained by so many observers that if the former case were ever to occur we should conclude that some hitherto unknown phenomenon had been met with, or that some error had been made in the measurements. In order to decide between these alternatives it would be necessary to make new

and still more careful experiments. Without the theory there would have been no reason for new and more accurate research. In general, after a theory (expressed concisely by means of a formula) has been verified in a great number of cases, it is of the highest practical value, for it permits us to calculate—much more accurately than we could determine experimentally—the magnitude of one of the quantities (*e.g.* the strength of current) represented in the formula, when the others are known. Thus theory is the greatest promoter of scientific research.

Returning to our consideration of Ohm's law, we find that it leads to researches on the influence of temperature, pressure, and time on the conductivity of different substances, and on the effect of dilution on the conductivity of electrolytes. In recent times such researches have resulted in the development of the theory of electrolytic dissociation. In this case Ohm's law was used, together with other laws deduced from van't Hoff's theory of the freezing-point of solutions.

Before a theory is established, we generally find an hypothesis used, which later on may develop into a theory. Such an hypothesis was, for instance, the assumption that it is the electromotive force (proportional to the number of cells used) that drives the electric current, which may be regarded as the motion of a substance through the conducting wires. (At the time of Ohm's discovery heat and electricity were regarded as matter.) All researches previous to Ohm's on the connection between the number of cells acting and the strength of the current must have been based on this hypothesis.

The work of Ohm transformed this rather vague and incomplete hypothesis into a law. *Quantitative* formulation, that is, the establishing of a connection, expressed by a formula, between different quantitatively measurable magnitudes, is the peculiar feature of a law or a theory. Of course, this is only valid for the so-called exact sciences, which deal with measurable *quantities*. A purely descriptive science develops to an exact one in so far as it introduces theories in the above sense, and it is just the development of chemistry in this direction in the last century which may be regarded as one of the best illustrations of our statement.

The introduction of statistical methods in biological science

as has been done in modern physiological researches on the development of living organisms, permits of the establishment of theories in these branches of knowledge. In biological sciences the word "theory" is often used in the same sense as hypothesis ; still, this has no influence upon our study of theories in exact sciences.

The main feature of a theory is, as we have just said, its bearing upon "quantities." It follows that measuring instruments must have been introduced before a theory can be established. In the case of Ohm's theory of the electric current, such an instrument was the galvanometer which had just been constructed by Schweigger.

According to the definition given above, the so-called phlogiston theory does not at all merit its name, for no instrument was devised for measuring the quantity of phlogiston, by the combination of which with the calces (oxides) metals were supposed to be produced. It was only an hypothesis which might have been developed into a theory, if some one had measured phlogiston, after working out a clear conception of its nature. Thus, for instance, it would have been possible to put the quantity of phlogiston given off on the oxidation of a metal equal to the quantity of heat developed during this process, the heat being measured calorimetrically. (In reality the old conception of phlogiston seems most nearly to correspond to this quantity of heat.) But instead of using a calorimeter, Lavoisier employed the balance for investigating the phenomenon of calcination ; and he found that just as much oxygen disappears during the calcination of a metal (he used tin, lead, and quicksilver) as the metal gains in weight.

He therefore propounded the theory that calcination consists of the combination of a metal with oxygen, and he demonstrated his theory by quantitative measurements. With this theory the old phlogiston hypothesis, lacking all quantitative foundation, did not agree, and was therefore given up.

The quantitative use of the balance resulted afterwards in the atomic theory of Dalton, of which the most important feature is the law of multiple proportions. This theory was a development of the atomic hypothesis of Democritus, which had already been known to science for about 2300 years.

As we have already seen, theories have a practical side of high importance in that they economize experimental work. We may compare the work of an investigator, who wishes to find the connection between two factors which are of influence upon natural phenomena, and who is not guided by a theory, with the work of an engineer, who wishes to connect two towns, situated on the opposite sides of a range of mountains, by means of a tunnel, and who breaks down a whole mountain in order to be sure of finding the shortest and easiest route. The scientific worker who uses a theory forms an opinion of the most convenient way of solving his problems. He is to be compared with the engineer who, by means of a preliminary survey, has formed an opinion of the relative positions of the two towns and of the mountain range, and with the aid of his instruments points out the direction on the two sides of the mountain in which his men have to bore the tunnel. If the opinion of the engineer is not quite correct, the tunnels from both sides will not meet precisely in the middle of the mountain, but the axis of the one will be distant some few feet from that of the other. Small corrections have then to be made at the point of intersection by widening the tunnel.

In the same way the theoretical considerations of the scientific worker may lead him a little astray; they must then be corrected slightly and improved. But from his quantitative measurements he finds the natural law which connects together the two factors examined. For building up his theory, the investigator has generally to carry out a series of preliminary measurements, in order to obtain a guiding hypothesis.

From what we have said, the extremely high value of theories will be clear. But theories should always be regarded only as a help, as an instrument or tool. Many, who are not acquainted with theoretical work, express the opinion that a theory should have the character of absolute truth and certainty. They say, for instance, that the emission theory of light has no value, because it has been replaced by the vibration theory of light; and when they hear that this theory also has lost its supremacy, being replaced by the electromagnetic theory of light, they shake their heads, and intimate that it would

have been better to have saved the time taken up in working out theories, and to have employed it in making experiments. Such persons fail to appreciate the fruitful use that Newton made of the emission theory, and the wonderful development of optics by means of the undulation theory. The opinion of these men is as well founded as that of a workman who rejects the use of tools because these will be replaced sooner or later by more refined machines.

Very often we hear the opinion expressed that a theory has little or no value, because it may be possible to build up another theory on other foundations. This is just as prudent as to recommend the giving up of an instrument in our possession because it perhaps might be possible to construct a better instrument out of another material, before the latter has been made and shown to do more or better work than the old one.

We have used the old method of comparing a theory with a tool or an instrument. One may then ask, "How should an hypothesis be represented according to this analogy?" An hypothesis may be compared with an instrument the name of which is characterized by the suffix "scope," *e.g.* electroscope, a theory being then compared with an instrument the name of which has the suffix "meter," *e.g.* electrometer. An electroscope enables us to decide if a body is charged with free electricity, and nothing more. The hypothesis has only a qualitative meaning, and tells us nothing about the quantity. Now, one may so elaborate an electroscope that an electrometer is obtained, *e.g.* by fixing a scale behind the gold leaves of the electroscope. We have then the electrometer of Hankel or of Exner. These are from an absolute standpoint somewhat imperfect electrometers, but they serve excellently for many purposes. The absolute electrometer and the quadrant-electrometer of Lord Kelvin may also be regarded as highly perfected elaborations of the gold-leaf electroscope.

In the same manner it is generally possible to work up an hypothesis into a theory by the help of quantitative measurement. Using the new theory, we make a large number of measurements in the new field and discover new connections between the various factors, or new rules that lead to new conceptions, *i.e.* to new hypotheses. These, on the other hand,

may thereafter be developed into new theories, which are connected with the old theory out of which they have arisen. These new theories may then be regarded as branches of the old one, and by working further in the same direction we elaborate a system of minor theories, which are all connected with the dominant theory. It is this development of theoretical work that characterizes modern exact science. As an example of such a theory which has developed an almost unlimited number of branches in different parts of physical and chemical science, we might cite the theory of the equivalence of different kinds of energy, or, as it is commonly called, the mechanical theory of heat.

The original hypothesis was in this case extremely simple, and may be stated as follows: "it is impossible to obtain perpetual motion, *i.e.* to construct a machine which performs work without consuming energy of any kind."

In Carnot's hands we see the first wonderful development of this hypothesis into a grand theory. This engineer officer had a practical end in view in his researches—he wished to develop a theory of the engines which transform heat into work, and which at that time had an ever-increasing importance. This work was forgotten, however, and we see how Mayer used the same hypothesis as Carnot, and worked out a theory of equivalence of heat and mechanical work. The work of Mayer was despised, and only a few scientists took notice of it. The same was the case with the simultaneous work of a Danish engineer Colding. But after these pioneers came a procession of theoretical philosophers, before all Joule, Helmholtz, Kelvin, Maxwell, and Clausius, who developed the theories of Carnot and Mayer, so that a theoretical system was built up which now dominates the whole of physical and a great part of chemical science. The greatest modern developments in this system are due to van't Hoff and Gibbs as far as chemical phenomena are concerned, and to Bartoli, Boltzmann, Wien, and Planck in the case of optical phenomena.

No other work has so strongly impressed its character upon modern science as this theoretical development. It is therefore wholly incomprehensible how the opinion can be expressed and find admiring auditors, that it would be better not to work

theoretically, but only to collect and register experiments. This opinion may be regarded as a repetition of Rousseau's maxim, that the uncivilized condition is the best for humanity.

In ordinary research work the *rôle* played by fancy is often very limited. Nearly all the attention is at first given to the exact determination of the experimental groundwork. When a sufficient number of data has been collected the theoretical development begins. Then the main point is to combine the results of the different experiments, finding out the common and general features, but leaving out those occasional peculiarities occurring in every experiment owing to unavoidable errors. In this work fancy plays the most important *rôle*, in that from an infinite number of possible combinations it must choose the most simple and most probable. Often the experiments are not exact enough, so that the occasional deviations wholly conceal the law that we seek. We may then use two different methods of procedure. The more rational one is to improve the methods of working, and especially to construct very accurate instruments, so that the experimental errors are reduced to a low value. But sometimes we cannot do this, especially in statistical work. We must then increase the number of observations. If we record forty observations, the experimental error of the mean is only half as great as that of the mean of ten observations, and that of a thousand observations is only the tenth part of that of ten. The experimental error of the mean is in general inversely proportional to the square root of the number of observations. As is evident, it is very laborious to reduce the experimental errors in this way, but sometimes it is the only practical method. If by these means we have found a real law, there will be a regularity in the deviations of the observed mean values from those calculated by its help, so that these differences decrease proportionally to the square root of the number of observations.

Some laws of Nature seem to be exactly true. Thus, for instance, experiments have been made to test the validity of Ohm's law within the widest possible limits, by changing the intensity of the current from the lowest value that we are able to measure exactly with the help of galvanometers, to the highest that we can obtain with the help of modern electrical

machines. The result has been that no deviation, greater than the experimental errors, could be detected. Other such laws are, for instance: the law of Newton for the attraction between material bodies; the corresponding law of Coulomb for electrical quantities; Snell's law of the refraction of light; and the two laws of thermodynamics.

But there is another class of laws, and these seem to be the more common; they are only valid within certain limits. As an example of such a law, that of Boyle or Mariotte may be considered. This law asserts that, if we enclose a given quantity of gaseous matter, for instance oxygen, in a vessel of variable volume (such as a cylinder in which works a piston), then the pressure of the gas is inversely proportional to the volume of the vessel. This is true for very low pressures, as Rayleigh<sup>1</sup> has demonstrated recently, but at higher pressures noticeable deviations occur. The first researches on Boyle's law did not lead to the observation of these deviations; hence it was thought that the law was exact. Further researches, carried out in the beginning of the nineteenth century by French savants, showed deviations, but these investigators were so convinced of the exactness of Boyle's law, that they overlooked the rather insignificant deviations which they had observed. As we now examine their experimental results, we find that nearly all the observed deviations were in the same direction, namely, that the observed pressure at small volumes was lower than that calculated. The nature of experimental errors is, however, that they fall as much in the one direction as in the other. Errors that fall in one direction only, are called systematic errors, and they are due to a definite cause, working always in the same direction. As now no reason for the occurrence of systematic errors can be detected in the present case, the investigators of the law of Boyle might have drawn the conclusion that it ceases to be exact at higher pressures. More accurate and wide-reaching work, especially that of Regnault, Natterer, and Amagat, showed well-marked regularities for these deviations. In this way scientists were led to seek for a new law, which agreed with Boyle's law at extremely low pressures and on the

<sup>1</sup> Rayleigh, *Trans. Roy. Soc.*, 1901, **196**, 205; *Proc. Roy. Soc.*, 1905, **74**, 446; *Phil. Trans., A.*, 1905, **204**, 351.

other hand showed no deviations from the experimental results at high pressures. Such a law was discovered by van der Waals, and it gave a startling insight into the physical nature of the gases.

But still further research made evident that the law of van der Waals does not cover all cases. With increasing experimental work, the general features of the deviations from van der Waals' law will probably soon be understood sufficiently for the formulation of a new law, by means of which we shall gain still more mastery over Nature than we now possess.

In this way theoretical work proceeds step by step, increasing our knowledge of Nature. If we have found a law which, like that of Boyle, is only valid within certain limits, it would be very unreasonable to say that it had no merit at all. Many of the wonderful applications of thermodynamics are based upon the assumption of the validity of Boyle's law. We have to seek the probable causes of the insufficiency of the law in question where the deviations are found, and to apply the necessary corrections, which will with time show themselves to be subject to another law, which completes the original law. In this manner scientific progress is made. The theoretical considerations indicate in which direction further work may be done with the greatest effect. Without them the advance would be very slow, or even impossible.

But the value of theoretical work is generally not limited to that particular part of science which is the direct object of the work in question. The example of Ohm's law shows us that the work of Fourier on the conduction of heat could, with little variation, be adapted to the explanation of the conduction of electricity. But the same law is, with suitable adaptations, also valid for the diffusion of dissolved matter, *e.g.* salts in a solvent, water. Here the dissolved substance flows from places of higher to those of lower concentration, just as heat flows from places of higher to those of lower temperature, or as electricity flows from places of higher to those of lower potential. The corresponding law of diffusion is called Fick's law, after its discoverer, and it has precisely the same form as that of Fourier or of Ohm.

Further, the benefit of theoretical researches is not confined

to the science in which they are carried out. Mathematics was already developed to a high degree in the early ages, and astronomy could use the results of that science, and in this way develop very early. The mathematical and astronomical knowledge of Galileo fitted him to lay the foundations of rational mechanics. Physics is a much more wide-reaching science than mechanics; in its own domain it utilizes the results of the work done in the latter science (*e.g.* the theory of potential), and has thus developed after the same plan. Chemistry is a still more extensive science than physics; it has adapted the laws of thermodynamics to explain phenomena in chemistry, and in the last quarter of a century has thereby won for itself a theoretical basis of the most wide-reaching character. In the same way the biological sciences, which have to do with much more complex phenomena than chemistry, have taken over modern theoretical methods from chemistry, and have in recent times made progress of the most promising character.

The solidity of the different branches of natural science is nowhere so evident as in the domain of theoretical research. All these sciences are highly interested in the theoretical work now going on in chemistry, which is not only raising this science to a higher scientific level, but also giving us a well-founded hope of increasing progress in neighbouring sciences, and especially in biology, which has the greatest importance for the development of humanity.

## CHAPTER II

### *OLD HYPOTHESES IN CHEMISTRY*

ANTIQUITY had a great antipathy to carrying out experimental work. It was not thought worthy of free men, but was an occupation for slaves. Philosophical contemplation, on the other hand, was held in high respect. Hence theories had very little chance of being elaborated, while hypotheses flourished. This feature is very clearly conspicuous in the work of Archimedes, who conceived the principle which bears his name, viz. that a body immersed in a liquid seems to lose just so much of its weight as the weight of the quantity of liquid displaced by it. He used this principle to determine what we should call the specific gravity of a crown, which he thus showed was not made of pure gold. He, however, apologizes for having carried out a piece of experimental research, which was work of very inferior value.

As far back as about 500 b.c., Empedocles had already introduced the notion that everything consists of four elements : earth, water, air, and fire. These elements of antiquity correspond more nearly to what we now call states of aggregation, if we except fire (which is equivalent to hot gases). Consequently Plato and Aristotle asserted that the elements might be converted one into the other. For instance, we read the following passage in Timaios : “We believe from observation that water becomes stone and earth by condensation, and wind and air by subdivision ; ignited air becomes fire, but this, when condensed and extinguished, again takes the form of air, and the latter is then transformed to mist, which resolves into water. Lastly, rocks and earth are produced from water.” To put it more simply, it had been observed that by cooling hot gases (“fire”), cool gases (“air”) were obtained, and that by condensation of

moist air one got water-drops, which might be united to give ordinary water. On the other hand, out of water were deposited solid substances, which had formerly been suspended or dissolved in the water. The ancient philosophers evidently only considered the *qualities* of the bodies, and therefore the hypothesis of the transformation of one element into another was a natural consequence. This hypothesis dominated the alchemistic view of the nature of substances. Again, the phlogiston hypothesis is only a variety of the transformation hypothesis. By adding something, that was called phlogiston, to the "calces" (oxides) of metals one obtained the metals themselves. Coal contained a large amount of phlogiston. Therefore, if one heated a metallic calx with coal, it combined with the phlogiston of the coal, and metal was the product. No attention was paid to the observation often made, that calcination, *i.e.* the driving out of phlogiston, was accompanied by an increase in weight.

Nevertheless, the old philosopher Empedocles had, on purely philosophical grounds, attained a standpoint which holds good even under modern criticism. Instead of the common doctrine, based upon observations of everyday life, that everything may be annihilated, and has a beginning and an end, he asserted that "nothing can be made out of nothing, and it is impossible to annihilate anything. All that happens in the world depends on a change of form and upon the mixture or the separation of bodies. An everlasting circulation is characteristic of Nature."

We find, also, that in the middle of the seventeenth century John Mayow expressed the idea that atmospheric air contains a substance which is also present in saltpetre, and which combines with metals to form their calces. The same substance is necessary for respiration, and converts venous into arterial blood.<sup>1</sup> Indeed, we find that Lavoisier used the balance<sup>2</sup> for making quantitative experiments, and he found that during the oxidation

<sup>1</sup> Mayow died in 1679, at the early age of thirty-four years. Probably this was the reason he did not obtain wider recognition for his ideas, which were soon forgotten. A century later, however, Lavoisier rediscovered and established the same principles, and caused the abandonment of the phlogistic hypothesis.

<sup>2</sup> As we have seen already, Archimedes had occasionally used the balance for quantitative research.

of a metal by air in a closed vessel the weight remained constant, *i.e.* "nothing can be created, and in every process there is just as much substance (quantity of matter) present before and after the process has taken place. There is only a change or modification of the matter."<sup>1</sup> The words are remarkably similar to those used by Empedocles, and they contain the law of the "conservation of matter" which has since been found to regulate all natural phenomena. But there is a great difference between Empedocles and Lavoisier. Empedocles did not indicate how the quantity of matter should be measured—his idea was only a diffuse philosophical one; whereas Lavoisier introduced the balance for measuring the quantity of matter, and by experiments upon different bodies, such as sulphur, phosphorus, mercury, lead, and tin, showed that his law was exact within the errors of experiment. We may therefore say that Lavoisier transformed the wonderful hypothesis of Empedocles into a scientific theory, which has since dominated physical and chemical science. Every analysis gives a new demonstration of the truth of Lavoisier's deductions. In recent times some researches have been carried out, especially by Landolt<sup>2</sup> and Heydweiller,<sup>3</sup> which seem to show that, in certain chemical processes, very slight deviations from the law of Lavoisier may be observed. These researches are not yet complete, and it has not yet been settled what may be the cause of these small deviations. It is possible that the vessels used, and which were made of glass or quartz, were not absolutely impervious to the substances formed during the chemical reactions. But there is still no sufficient ground to suppose that after a thorough and critical discussion of the results of these interesting researches the theory of Lavoisier will be overthrown.

Just as Empedocles had enunciated the hypothesis which was afterwards developed into a theory by means of Lavoisier's quantitative researches, so the so-called Dalton's theory of multiple proportions was preceded by an hypothesis of the philosopher Democritus. This remarkable man propounded the

<sup>1</sup> Lavoisier, "Traité de Chimie," Œuvres, vol. i. p. 101.

<sup>2</sup> Landolt, *Zeit. physikal. Chem.*, 1893, **12**, 1; 1906, **55**, 589.

<sup>3</sup> Heydweiller, *Physikal. Zeit.*, 1900, **1**, 527; 1902, **3**, 425; *Ann. Physik.*, 1901, **5**, 394.

idea that bodies are built up of indefinitely small indivisible particles, which he called atoms. These are distinguished from each other by their form and size, and also by giving different products when differently aggregated. This bold conception remained in the hypothetical stage for about 2300 years, as no quantitative conclusions were drawn from it till the time of Dalton. It seems as if the idea of Democritus prevailed over the seemingly more simple idea that everything may be divided indefinitely, and which was preferred by most of the purely philosophical investigators.

The atomic hypothesis of Democritus was revived by the physicist Gassendi about the year 1650. It was then also accepted by such eminent authorities in physics and chemistry as Newton and Boyle. Boyle had the great merit of giving to the notion "element" a more exact meaning, which nearly corresponds with the modern one, and has a great advantage over the fluctuating one of antiquity as given in Aristotle's works. Boyle criticized the opinions of Aristotle and of the alchemists, and showed that only the undecomposable constituents of matter (and not, for instance, the changeable qualities of matter) should be called elements. According to Boyle's opinion, these elements consist of minute particles, which attract one another, and, after combination, form the different chemical compounds.

In the history of chemistry the substances which we call acids, bases, and salts always played a most important rôle. These substances react more regularly than other bodies, and in their reactions usually new substances of the same class are formed. Therefore these substances, which commonly occur in inorganic nature or may easily be formed from natural products, were among the first to be chemically investigated. Wenzel and Richter studied the laws according to which acids and bases neutralize one another in forming salts. They found that the acids and the bases always combine in constant so-called "stoichiometric" proportions. Richter also asserted that "when equal amounts of the same acid are rendered neutral by different amounts of two or more bases respectively, the latter are equivalent to one another, and *vice versa*." We find, according to Richter, the same equivalent numbers for different

bases, whether we use nitric, hydrochloric, sulphuric, or any other acid.

The eminent Swedish chemist Scheele had discovered that many metals (iron, copper, and mercury) are subject to different stages of oxidation. Richter now drew the conclusion that the quantities of an acid which are bound by different oxides (in their salts) are proportional to the quantities of oxygen contained in them. Then he came naturally to the conclusion that the two oxides of iron or of mercury respectively contain oxygen in two constant proportions.

This peculiarity of constant proportions is characteristic of chemistry in contradistinction to physics, where the more simple continuous and gradual transition prevails, *e.g.* for mixtures of alcohol and water. Therefore it will not seem astonishing to us that a chemist like Berthollet, who was very well acquainted with the more highly developed physical science, adhered to the opinion that chemical compounds (*e.g.* the nitrates of mercury) behave just as mixtures, so that the ingredient elements in them may be varied continuously. (The work of Richter was very little known at that time.) A fellow-countryman of Berthollet, Proust, at the end of the eighteenth century, carried out work of remarkable exactitude, by which he proved that in the compounds which tin forms with oxygen, or in the compounds of iron with sulphur, the quantity of oxygen or sulphur does not vary gradually, but by leaps, so that there exist (according to him) only two definite compounds of tin with oxygen, and two of iron with sulphur. He also revised the work of Berthollet, and showed that his compatriot had dealt with mixtures, and not with definite chemical compounds. The brilliant ideas of Berthollet were afterwards revived by the researches of the Norwegian chemists, Gulberg and Waage, on the law of chemical mass-action.

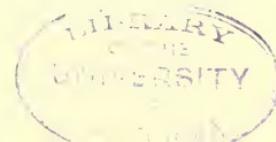
Proust came very near to the discovery of the law of multiple proportions. If he, for instance, had calculated the quantities of oxygen which are combined with a unit-weight of tin in both its oxides, or of sulphur combined with one unit weight of iron in both its sulphides, he would probably have been led to the discovery of the law which now bears the name of Dalton. This English physicist and chemist was led,

by consideration of the behaviour of the gases of the atmosphere,<sup>1</sup> to investigate the relative weights in which these gases and other elements combine with each other in their compounds. His experimental work was not very accurate, as we may see from his figures, but his talent for abstraction led him in the right direction. If we use the modern symbols introduced into chemistry by Berzelius, to which Dalton, curiously enough, was strongly opposed, favouring his own much more inconvenient symbols, and if we let N represent 4 unit-weights of nitrogen, O 5·66 of oxygen, H 1 of hydrogen, C 4·5 of carbon, and S 17 unit-weights of sulphur, Dalton showed, as a result of his experimental work (1803), that the following compounds had the composition given :—

Nitrous oxide, N <sub>2</sub> O	Ammonia, NH
Nitrous gas, NO	Oxide of carbon, CO
Nitrous acid, N <sub>2</sub> O <sub>3</sub>	Carbonic acid, CO <sub>2</sub>
Nitric acid, NO <sub>2</sub>	Sulphurous acid, SO
Water, HO	Sulphuric acid, SO <sub>2</sub>
Marsh gas, CH <sub>2</sub>	Olefiant gas, CH

It is easy to see that there are rather large experimental errors in these data, if we compare them with what we know now to be the real compositions of these substances. Later on Dalton improved his figures (1808), and put the combining weight of oxygen as 7 instead of 5·66, and that of carbon as 5 instead of 4·5, but they still were far from exact. "Nevertheless," as Roscoe rightly observes in his work on Dalton, "in spite of his rough methods of experimentation, Dalton's results stand out the greatest landmarks in our science." The general and diffuse hypothesis of Democritus had here taken a concrete form, and was converted into a theory, according to which we may calculate the relative quantities of chemical elements which enter into combination with each other. The atoms of chemical elements possess weights which are proportional to numbers contained in tables of atomic weights, and chemical compounds consist of groupings of a certain whole number (in inorganic chemistry a low number) of one kind of atom with a certain

<sup>1</sup> Cf. "New View of Dalton's Atomic Theory," by Roscoe and Harden. Macmillan : 1896.



whole number of another kind, and of a third kind, and so forth. Since the number of the atoms in chemical compounds only varies as simple whole numbers, there cannot be a continuous change from one compound to another made up of the same elements. The quantities of one element which are combined with the unit-weight of another element are, therefore, in the ratio of simple whole numbers.

The theory of Dalton was soon found to be of the greatest value to chemical science, and it was confirmed by the rapidly increasing experimental results in this science, especially those obtained by the great leader of chemistry at that time, Berzelius. He determined the atomic weights with such exactitude, that they have remained almost unchanged from his time till now.

It follows, from the theory of Dalton, that the atomic weights of the elements are discrete numbers, between which no continuous transition exists. Prout put forward the idea, that if we put the atomic weight of hydrogen as unity the other atomic weights are whole numbers, so that the atoms might possibly all be regarded as built up of hydrogen atoms. Already the work of Berzelius showed the hypothesis of Prout to be untenable, but nevertheless this hypothesis seemed so pretty from a philosophical standpoint, that many scientists have attempted to verify it. Indeed, many atomic weights do not differ much from whole numbers, if we take that of hydrogen as unity. But the very accurate work of Stas, and in later times of Lord Rayleigh<sup>1</sup> and others, proves with certainty that the atomic weights of chlorine and oxygen cannot be made to agree with Prout's hypothesis.

A very original foundation of a similar hypothesis was given some thirty years ago by Lockyer, on astronomical grounds. The spectra of the hottest stars seem to indicate that they consist chiefly of hydrogen. On the other hand, the spectra of the sun and other celestial bodies which do not belong to the hottest kind of stars, show the hydrogen lines much weakened and accompanied by the lines of many other elements. Now, it is natural to suppose, and this view is confirmed by stellar spectrum analysis, that matter is fairly uniformly distributed in

<sup>1</sup> Rayleigh, *Phil. Trans.*, A, 1905, **204**, 351.

the universe. Hence Sir Norman Lockyer<sup>1</sup> was led to enunciate the idea that at very high temperatures all elements are decomposed into hydrogen atoms. But the most recent researches seem to indicate that stars which are still hotter than the hydrogen stars chiefly contain the newly discovered element helium (and also oxygen). It seems, therefore, impossible to carry through the bold idea of Lockyer. There seem to be some indications—according to the brilliant discoveries of Sir William Ramsay<sup>2</sup>—that the new element radium decomposes spontaneously into helium and perhaps other elements. The quantities of helium obtained in this manner are, however, so exceedingly small that it seems prudent to await the results of further researches on this very interesting point before we abandon the idea, confirmed by all other experimental work in chemistry up to the present day, that the substances which are shown to be simple elements by spectrum analysis are indestructible.

As Rutherford remarks in his Bakerian lecture (1904), if we assume that radium is converted into helium with such a speed that the half of it remains after 800 years, as the measurements of the helium quantity evolved indicate, then, if the earth had originally consisted of pure radium, after 16,000 years only the millionth part of it would be so constituted, and it would not be richer in radium than a good specimen of pitch-blende. After a further 16,000 years its radio-activity would scarcely be perceptible.

Now, geologists agree in the opinion that the earth has existed under conditions fairly similar to the present during many millions of years. It must, therefore, seem very strange that any radium exists at the present time, if we do not suppose that there is some source from which new quantities are produced. It is now believed that this source might probably be found in the minerals containing uranium, which also contain helium and radium. It may here be remarked that different uranium minerals contain radium in very different quantities—as the investigations of Mme. Curie indicate—and this was just the reason for searching for a new element (later called radium) in the most radio-active one of them, namely,

<sup>1</sup> Lockyer, *Beiblätter*, 1879, **3**, 88.

<sup>2</sup> Ramsay and Soddy, *Proc. Roy. Soc.*, 1903, **72**, 204.

pitch-blende. If all minerals containing uranium were decomposed into radium at the same rate (and all specimens of radium disintegrated with the same velocity of reaction), then we might expect that all minerals containing uranium would contain the same relative content of radium.

The recent investigations of Strutt,<sup>1</sup> Boltwood,<sup>2</sup> and Soddy<sup>3</sup> seem, indeed, to indicate, that the quantities of uranium and radium present in the most different minerals bear a constant ratio to each other. (Some deviations which exist can be explained by the partial extraction or deposition of the radium salt.) Boltwood and Rutherford<sup>4</sup> have determined the equilibrium to be  $1.35 \times 10^6$  molecules of uranium to every molecule of radium. Experiments of Rutherford to obtain radium from thorium or actinium were not successful.

After a number of unsuccessful endeavours, Soddy<sup>5</sup> says that he has been able to prove the presence, after 567 days, of  $1.6 \times 10^{-9}$  grm. radium, as measured by the strength of the emanation, in 1 kilogram of dissolved uranium nitrate, which had been previously freed from radium by precipitation of barium sulphate. This quantity is a thousandth part of the quantity calculated from the known velocity of change of uranium. Judging from his own experience, Boltwood<sup>6</sup> considers the result of Soddy to be "doubtful." Using a method similar to Soddy's, he was not able to detect any radium in 100 grams uranium nitrate after 390 days, although he would have been able to detect one-tenth of the quantity which should have resulted according to Soddy. There is no doubt that a decision will soon be arrived at in the matter.

<sup>1</sup> Strutt, *Proc. Roy. Soc.*, 1904, **76**, 88.

<sup>2</sup> Boltwood, *Sill. Journ.* (4), 1904, **18**, 97; *Phil. Mag.* (6), 1905, **9**, 599.

<sup>3</sup> Soddy, *Phil. Mag.* (6), 1905, **9**, 768.

<sup>4</sup> Rutherford and Boltwood, *Sill. Journ.* (4), 1905, **20**, 55. G. von dem Borne (1906) comes to the conclusion that in the rocks investigated by him, "there is no sign of proportionality between uranium content and radioactivity."

<sup>5</sup> Soddy, *loc. cit.*

<sup>6</sup> Boltwood, *Sill. Journ.* (4), 1905, **20**, 239.

## CHAPTER III

### *EXISTENCE OF HYDRATES IN SOLUTION*

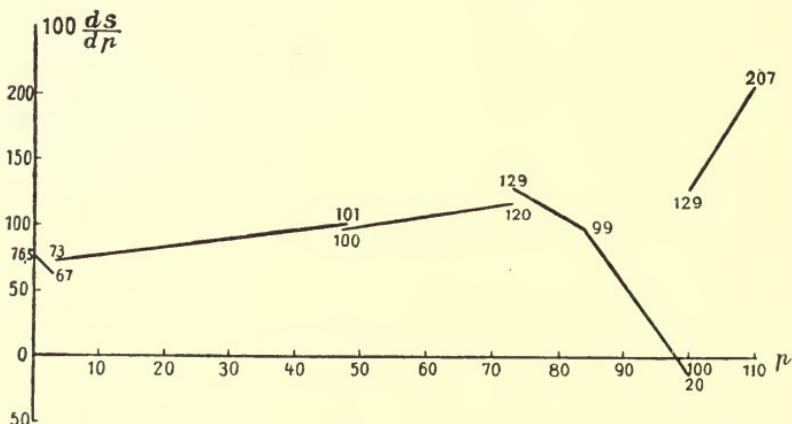
EXPERIENCE has shown the working chemist that between the different chemical elements (and the same may be said also of compounds) no continuous and gradual transitions are possible. This idea has grown so familiar to chemists that they have often looked for discontinuities in the domain of physical chemistry, only to find, on closer investigation, that nothing of the kind exists.

The most extensive researches of this kind were made on aqueous solutions, and their tendency was to show that some properties of a solution change discontinuously at certain points, corresponding to mixtures of definite quantities of water with a given quantity of the dissolved substance. These mixtures correspond to a definite molecular formula for a hydrate (1 subst. +  $n\text{H}_2\text{O}$ ), and the investigators made the supposition that these hydrates exist in solution.

This view has received the name *hydrate theory of solutions*, and as it has been supported by very eminent chemists, among others very strongly by Mendeléeff, it seems well worth while to examine it a little more in detail. Mendeléeff<sup>1</sup> determined the specific gravity of solutions of sulphuric acid. As is well known, this property ( $s$ ) increases with the concentration ( $p$ ). This percentage rate of increase  $\left(\frac{ds}{dp}\right)$  Mendeléeff calculated from his determinations, and deduced the following equations, which are geometrically represented in the diagram. As we see from these equations, and still better from the diagram, Mendeléeff represented this increase by six different straight lines, showing

<sup>1</sup> Mendeléeff, *Zeit. physikal. Chem.*, 1887, 1, 275.

no continuity where they meet.<sup>1</sup> From this he concluded that the solutions in which these discontinuities occurred represented chemical compounds of sulphuric acid with water, the composition being  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 + 150\text{H}_2\text{O}$ . If  $p$ , i.e. the concentration of the sulphuric acid, is greater than one hundred, this represents a solution of  $\text{SO}_3$  in  $\text{H}_2\text{SO}_4$ . A closer inspection of the curve shows that the discontinuity at  $p = 47.5$  (corresponding to  $\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$ ) is very insignificant, so that



$$\begin{aligned}
 100 \frac{ds}{dp} &= -651 + 7.8p \quad (p = 100 - 110\%) \\
 &= 728.76 - 7.49p \quad (p = 84 - 100; n = 0 - 1) \\
 &= 326.7 - 2.71p \quad (p = 73 - 84; n = 1 - 2) \\
 &= 61.9 + 0.8p \quad (p = 47.5 - 73; n = 2 - 6) \\
 &= 71.2 + 0.41p \quad (p = 3.5 - 47.5; n = 6 - 150) \\
 &= 76.5 - 2.65p \quad (p = 0 - 3.5; n = 150 - \infty)
 \end{aligned}$$

FIG. 1.—Density of solutions of sulphuric acid (Mendeléeff).

it would be wholly incorrect to draw any conclusions from its existence. The same may be said of the discontinuity at  $p = 3.5(\text{H}_2\text{SO}_4 + 150\text{H}_2\text{O})$ . There remain only the hydrates  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , and  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ . These compounds we are able to produce in solid form, and it is therefore very probable that they exist also in solution, it may be in a partially dissociated state. Therefore the laborious analysis of Mendeléeff only indicates the probability that both these

<sup>1</sup> The original curve of Mendeléeff in *Zeit. physikal. Chem.*, vol. i, p. 275, does not give a very accurate representation of his numerical data, therefore I have reconstructed the curve from his equations and given it above.

hydrates and  $\text{H}_2\text{SO}_4$  exist to some extent in solution. For obtaining definite results we must examine other properties of solutions of sulphuric acid, as, for instance, their conductivities for electricity and their freezing-points.

Of the first property F. Kohlrausch<sup>1</sup> has made very accurate determinations at 18° C., the results of which are given below:—

% $\text{H}_2\text{SO}_4$ .	Conductivity.	% $\text{H}_2\text{SO}_4$ .	Conductivity.
1	0·0429	75·0	0·1421
5	0·1952	80·0	0·1032
10	0·3662	84·0	0·0915
20	0·6108	86·0	0·0926
30	0·6912	90·0	0·1005
40	0·6361	92·0	0·1030
50	0·5055	94·0	0·1001
60	0·3487	96·0	0·0885
70	0·2016	99·4	0·0080

We see here four different solutions with characteristic features, namely, two maxima at 30 and 92 %, and two minima at 84 and nearly 100 %. (W. Kohlrausch<sup>2</sup> found that the last minimum is at 99·75 %.) The two minima mark the hydrates  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$ , of which the existence is therefore very probable. The two maxima coincide approximately with the hydrates  $2\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$  (30·4 %) and  $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  (91·6 %). Now, Kohlrausch has given the rule that pure chemical compounds have a lower conductivity than solutions. Therefore it seems very probable that both minima of electrical conductivity correspond to simple chemical compounds. But there is no such rule valid for maxima of conductivity, and hence we have no ground for concluding from the conductivity that such compounds as  $2\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$  and  $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  exist (in liquid form). For  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4 + 150\text{H}_2\text{O}$  (at 73 % and 3·5 %), the conductivity indicates no singularity. We may, therefore, say that a comparison of Mendeléeff's and Kohlrausch's experimental researches leads

<sup>1</sup> F. Kohlrausch, *Ann. Physik. u. Chem.* (3), 1885, **26**, 161.

<sup>2</sup> W. Kohlrausch, *Ann. Physik. u. Chem.* (3), 1882, **17**, 69.

to the conclusion that only the two hydrates  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  exist undissociated in liquid form.

Pickering<sup>1</sup> revised Mendeléeff's data for the specific gravity, and found that in the  $\frac{ds}{dp}$  curve there are no discontinuities, but only abrupt changes of direction.

The least ambiguous evidence on this question was given by Jones<sup>2</sup> in his research on the freezing-points of mixtures of sulphuric acid and water in acetic acid as solvent. From the researches of Raoult and others, we know, that if we dissolve one gram-molecule of any substance in a given quantity of acetic acid, it lowers the freezing-point just as much in all cases, independently of the nature of the added body. Two gram-molecules give double the lowering, and so on. We might, according to Raoult's law, expect that, if we add A parts of water to one litre of acetic acid, and the lowering of the freezing-point is  $a^\circ \text{ C.}$ , and if we dissolve B parts of sulphuric acid in another litre of acetic acid, and this gives the lowering  $b^\circ \text{ C.}$ , the solution of A parts water and B parts of sulphuric acid would give a freezing-point  $(a + b)^\circ \text{ C.}$  lower than that of acetic acid.

The following table gives some of Jones' observations on mixing the quantities B grams of sulphuric acid with 26.335 grams of acetic acid and 0.753 gram (A) of water. The water alone would give a depression ( $a$ ) of  $4.69^\circ \text{ C.}^3$  By special experiments the lowering ( $b$ ) caused by the sulphuric acid alone was found, and likewise the lowering ( $c$ ) by A + B was experimentally determined. The difference  $(a + b) - c = d$ .

B.	b.	c.	a.	$a + b$ .	d.
0.109	0.185	4.474	4.690	4.875	0.401
0.224	0.330	4.263	4.670	5.000	0.737
0.447	0.585	3.850	4.645	5.230	1.380
0.679	0.795	3.540	4.615	5.410	1.870
1.209	1.215	3.002	4.565	5.780	2.778
1.654	1.580	2.734	4.545	6.085	3.351

<sup>1</sup> Pickering, *Chem. News*, 1889, 59, 248; *Zeit. physikal. Chem.*, 1891, 7, 378.

<sup>2</sup> Jones, *Zeit. physikal. Chem.*, 1894, 13, 419.

<sup>3</sup> At higher values of B, the lowering  $a$  was supposed to be inversely proportional to the total volume, in accordance with the gas laws.

B.	b.	c.	a.	a + b.	d.
2·349	2·020	2·607	4·475	6·495	3·888
3·119	2·600	2·752	4·410	7·010	4·258
3·829	3·185	3·037	4·345	7·530	4·493
4·520	3·840	3·495	4·295	8·135	4·640
5·218	4·510	4·032	4·235	8·745	4·713
5·927	5·160	4·713	4·190	9·350	4·637
6·632	5·825	5·383	4·130	9·955	4·572

0·753 gram of water is equivalent to 4·22 grams of sulphuric acid as regards the lowering of the freezing-point. If we add more than 4·22 grams of sulphuric acid, and the combination  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  is formed, we should expect all the water to disappear from the solution, and since one molecule ( $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ) is formed by every molecule  $\text{H}_2\text{SO}_4$ , the lowering should be exactly the same as if no water were added, *i.e.*  $c$  would equal  $b$  if  $B$  is greater than 4·22. This is the case;  $c$  is approximately equal to  $b$ , being just a little less (about 10%). This result indicates that about 90%<sup>1</sup> of all the water molecules each bind one molecule of sulphuric acid, giving ( $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ), and the remaining 10% of the water-molecules each combine with two molecules  $\text{H}_2\text{SO}_4$ , in this manner forming the more complex molecule ( $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ).

We may now examine whether this is also the case when we have added half as many molecules of sulphuric acid as the number of water-molecules present. This occurs as soon as  $B$  is equal to 2·11 (we may use the figures for the neighbouring value  $B = 2\cdot349$ ). Here we observe that  $c$  is greater than  $b$ —in other words, all the water-molecules are not bound to sulphuric acid in the form  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , but part of them are free (about 30%), and dissociated into ( $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ) and  $\text{H}_2\text{O}$ . From these results we conclude that the hydrate  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  is less stable than  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , but that it exists in great quantity (about 70%) in solutions of the composition  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  (73%  $\text{H}_2\text{SO}_4$ ). Further, we may conclude that in mixtures which contain less than 2·11 grams of  $\text{H}_2\text{SO}_4$ , just double the number of molecules of water should disappear from the solution

<sup>1</sup> On account of the deviation of concentrated solutions from van't Hoff's law, this percentage must not be considered to be very accurate.

—to give molecules  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ —as the number of the  $\text{H}_2\text{SO}_4$  molecules added, supposing that the hydrate  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  is formed. Therefore  $d$ , which is proportional to the number of water-molecules bound by the sulphuric acid, ought to be twice as great as  $b$ , which itself is proportional to the number of  $\text{H}_2\text{SO}_4$  molecules present. This is approximately the case;  $d$  is not only twice as great as  $b$ , but a little greater—but always less than three times  $b$  (about 2·25 $b$ ). We learn from this that with excess of water there may probably exist (to the extent of about a third of the molecules  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  present) a higher degree of hydration, such as  $\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$ . In these researches the presence of the acetic acid interfered somewhat, and we might therefore expect that in mixtures of water and sulphuric acid (without acetic acid) the hydrates would be more stable. Jones' further researches seem to show that this is the case.

If we summarize the results of Jones' experiments, we find that the hydrate  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$  is very stable, and is found in solutions which contain more molecules of  $\text{H}_2\text{SO}_4$  than of  $\text{H}_2\text{O}$ . Together with this stable hydrate there are indications that a lower hydrate, probably  $2\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , also exists to a slight extent in the same solutions. If more water is added, molecules of a new hydrate,  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , are formed, which is also very stable, but not so much so as the hydrate  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ . In the solution  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$  (73%  $\text{H}_2\text{SO}_4$ ) about 70% of the molecules have a composition agreeing with this formula. The remainder of the sulphuric acid may occur as molecules having the composition  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ , and a correspondingly smaller proportion (15%) of the water-molecules are free. At higher dilutions it seems as if nearly all the sulphuric acid were converted into the complex  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ , and if there is enough water present, one-third into a higher hydrate, perhaps  $\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$ .

The higher hydrates containing still more water, e.g.  $\text{H}_2\text{SO}_4 + 6\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 + 150\text{H}_2\text{O}$ , the existence of which different workers had deduced from their researches, do not seem to exist.

Mendeléeff<sup>1</sup> supposed hydrates to exist in mixtures of water

<sup>1</sup> Mendeléef, *Journ. Chem. Soc.*, 1887, 25, 778.

and alcohol, using the same method for indicating them as in the case of aqueous solutions of sulphuric acid. These hydrates were stated by Mendeléeff to have the composition  $3C_2H_6O + H_2O$ ,  $C_2H_6O + 3H_2O$ , and  $C_2H_6O + 12H_2O$ . Jones<sup>1</sup> has also investigated these hydrates in the same manner as for sulphuric acid, and he found no evidence of their existence. Conclusions as to the existence of salt hydrates have also been drawn from the freezing-point of solutions. In these cases also a closer examination shows the conclusions to lack trustworthiness. These cases will be considered later.

From these examples we see how it is possible to deduce the existence of hydrates from the physical properties of solutions. But we also see that many of the discontinuities which Mendeléeff thought he had found, and which he used for demonstrating the existence of hydrates in solution, cannot be said to have a real existence when subjected to a critical examination. The same is also true for most of the hydrates which have been thought to exist, because of the occurrence of maxima and minima in other physical properties. For instance, it was found that at 0° C. the viscosity of solutions of ethyl alcohol in water has a maximum at a concentration of about 36 %, corresponding to a composition of  $2C_2H_5OH + 9H_2O$ . From this fact it was concluded that this hydrate of alcohol exists. But a closer investigation showed that the point at which the maximum of viscosity occurs changes very considerably with the temperature. At 17° it occurs at 42 %, corresponding to  $2C_2H_5OH + 7H_2O$ , and at 55° at 50·5 %, corresponding to  $2C_2H_6O + 5H_2O$ . It is therefore evident that it is impossible to maintain the idea that a hydrate  $2C_2H_5OH + 9H_2O$  exists as a chemical compound at 0°, for at other temperatures we should then be compelled to assume hydrates such as  $2C_2H_5OH + 5H_2O$  at 55°, and at intermediate temperatures we must then accept hydrates of any composition between  $2C_2H_5OH + 9H_2O$  and  $2C_2H_5OH + 5H_2O$ . An analogous case occurs with acetic acid, but there the change is rather small; from 79 % at 0° to about 77 % at 60°. The composition 77 % corresponds to the formula  $CH_3COOH + H_2O$ .

<sup>1</sup> Jones, *Zeit. physikal. Chem.*, 1894, **13**, 419.

Now, it is a general rule, as I<sup>1</sup> have found, that the addition of a non-electrolyte to water increases the viscosity of the latter. Therefore, if the non-electrolyte has a lower viscosity than water, there must be some intermediate solution, the viscosity of which is a maximum. The same is also valid if the non-electrolyte has a viscosity which is not very much greater than that of water, for instance ethyl alcohol, of which the viscosity at 0° is greater than that of water by only 2·1 %. There are some such non-electrolytes, for instance acetone and methyl alcohol, which are soluble in water in all proportions. If the maximum of viscosity indicated a hydrate, we could conclude that all these substances possess at least one definite hydrate, without knowing anything more of them than that they are soluble in water. From this circumstance alone, it is evident that no such conclusion can be drawn.

The same holds for the conductivities of electrolytes. According to a rule given by Kohlrausch, pure substances have a low conductivity, but their solutions in water conduct very well. Pure water and pure acetic acid, for example, are very bad conductors of electricity, but solutions of acetic acid in water conduct fairly well. Therefore some particular solution of acetic acid must possess a maximum conductivity; this solution contains 16·6 % acetic acid at 18°C., corresponding to the formula  $\text{CH}_3\text{COOH} + 16\cdot7 \text{ H}_2\text{O}$ . From this fact it would not be correct to infer the existence of a hydrate, say of the composition  $\text{CH}_3\text{COOH} + 17\text{H}_2\text{O}$ . Very many electrolytes exhibit such a maximum conductivity, and it is no more correct to infer the existence of hydrates in these cases than in the case of acetic acid.

In the study of vapour tensions real breaks or discontinuities are often found. Thus, for instance, the vapour tension of ice below, and that of water above zero are represented by two curves which at their common point (0° C.) meet with the formation of an obtuse angle, *i.e.* the curve shows a break. The reason of this is that the volatile body is different in the two cases, namely, ice and water. Water may be undercooled and its vapour pressure measured below 0° C. The results of these measurements give a curve which is continuous (showing no break)

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1887, 1, 285.

with the curve above zero. The acute angle between the curve of the vapour pressure of water below 0° C. and that of the vapour pressure of ice is proportional to the latent heat of fusion of ice (per gram-molecule).

The modern theory of solutions asserts that the solubility of a substance is analogous to its vapour tension, and we might, therefore, expect breaks to occur in the solubility curves, similar to those found in the vapour-tension curves. This is indeed the case. A classical example is the solubility of sodium sulphate, the stable modification of which, below 32·5° C., crystallizes with ten molecules of water ( $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ ), and above this temperature without water of crystallization. The following table gives the solubility ( $g$ ) in grams of anhydrous  $\text{Na}_2\text{SO}_4$  dissolved in 100 grams water at the corresponding temperature ( $t^\circ \text{ C.}$ );  $m$  is the solubility expressed in gram-molecules per litre:—

$t.$	$g.$	$m.$	$t.$	$g.$	$m.$
0	4·40	0·31	50	46·2	2·92
10	8·98	0·63	60	45·3	2·83
20	19·1	1·32	70	44·1	2·75
30	41·1	2·63	80	43·3	2·69
32·5	49·6	3·11	90	42·6	2·64
40	48·2	3·01	100	42·2	2·60

At the "transition-point," 32·5° C., there evidently occurs a break in the curves representing  $g$  or  $m$  (see Fig. 2). These curves rise continuously till the temperature 32·5° is reached, and afterwards fall with increasing temperature. This break corresponds to the latent heat, which is used up when ten molecules of water are expelled from the crystals of  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  into the saturated solution.

It would be wholly incorrect to conclude, from the occurrence of these breaks, that the solution consists of a definite hydrate, in this case composed of 49·6 grams  $\text{Na}_2\text{SO}_4$  and 100 grams water, corresponding approximately to the formula

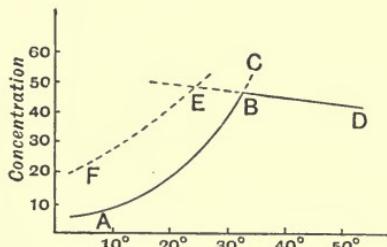


FIG. 2.

$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ . On the contrary, the correct conclusion is, that the break in the solubility curve denotes that below the corresponding temperature the solubility of one particular solid substance ( $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$ ), and above it the solubility of another solid substance ( $\text{Na}_2\text{SO}_4$ ), has been measured. Of the hydrates which may possibly be contained in the solution, the break tells us nothing. .

A similar case occurs in the freezing-point of solutions. If any solution, on cooling, deposits a solid compound of exactly the same composition as the solution, the freezing-point for this particular solution is a maximum. Thus, for instance, if we freeze a solution of sodium chloride, the freezing-point is a maximum ( $0^\circ \text{ C.}$ ) when the solid body separating out (pure ice) has the same composition as the solution. This is the case for pure water, which has a higher freezing-point than solutions of sodium chloride. The same is true for a solution of 47·06 grams  $\text{SO}_3$  in 100 grams water, corresponding to the composition  $\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$ . This solution freezes at  $-25^\circ \text{ C.}$  Solutions of higher or lower concentration (between 31 and 55 %) have all lower freezing-points, as is shown in Fig. 3, which is copied from Meyerhoffer, *Physikalisch-chemische Tabellen*, p. 567. This has been supposed to indicate that the solution corresponding to the composition  $\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$  should be regarded as a homogeneous substance, from which the same substance crystallizes out in the solid form. But in reality it only proves that the hydrate  $\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$  freezes out from solutions of the said composition. The curve shows similar maxima for pure water,  $\text{H}_2\text{SO}_4 + 2\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{SO}_4 + \text{SO}_3$  in regions where these compounds separate out in the solid form. Doubtless there also exists another maximum, viz. for  $\text{SO}_3$ .

The minima in the curve represent solutions from which so-called cryohydrates separate out, *i.e.* mixtures of the two solid bodies which separate out at higher and lower concentrations (*vide* below). Thus, for instance, the point B, corresponding to a solution of 31 grams  $\text{SO}_3$  in 100 grams  $\text{H}_2\text{O}$  and a temperature of  $-75^\circ \text{ C.}$ , is characterized by the freezing out of pure ice and  $\text{H}_2\text{SO}_4 + 4\text{H}_2\text{O}$  in such proportions that the composition of the liquid remains unchanged. There is evidently

no ground to conclude that in this case the solution consists of one kind of molecule only— $3\text{H}_2\text{SO}_4 + 40\text{H}_2\text{O}$ . All these maxima and minima tell us nothing of the composition of the molecules in the liquid; they only indicate the composition of the substances which freeze out.

Special interest has been awakened by those mixtures which do not alter in composition, as they change from one

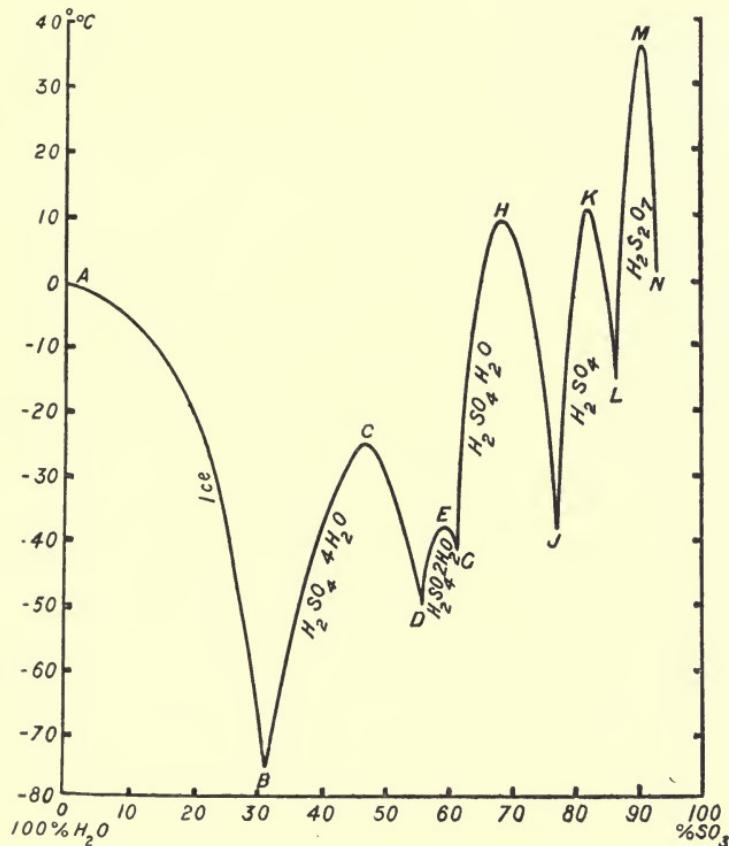


FIG. 3.—Freezing-points of sulphuric-acid solutions (Meyerhoffer).

state of aggregation to another. To this category belong the so-called cryohydrates, of which we have given some instances above. If we have a weak solution of sodium chloride in water and subject it to a low temperature, water freezes out in the form of ice from the solution. By this process the concentration of the solution is increased, and therefore its freezing-point sinks. This goes on until the solution becomes saturated with

sodium chloride. If, then, more ice freezes out from the solution, its saturation-point is exceeded, and therefore a corresponding quantity of the salt must also separate, so that the solution remains saturated. In other words, the concentration of the solution remains unchanged (saturated solution), and therefore the mixture of salt and ice which separates from it must also have the same composition, and the freezing-point becomes constant. This occurs at  $-21.3^{\circ}$  C., at which temperature the saturated solution has a composition of 35.5 grams of salt to 100 grams of water. This composition corresponds to the formula  $\text{NaCl} + 9\text{H}_2\text{O}$  very nearly. On the other hand, if we had had a solution which contained more salt, say 37.5 parts of salt to 100 parts of water at  $100^{\circ}$ , and had cooled this solution, it would become saturated at a temperature of about  $70^{\circ}$ . On further cooling, salt crystals would separate out, since the solubility decreases as the temperature falls. This would go on till the temperature became  $-21.3^{\circ}$  C. Then the saturated solution would contain 35.5 parts of salt to 100 parts of water, just as in the preceding case, and consequently after that, a mixture of the same composition would freeze out at the constant temperature of  $-21.3^{\circ}$  C. In this way we find that on cooling any solution of sodium chloride either ice or salt commences to separate out, and it finally freezes without changing its composition. Constant composition was usually regarded as a proof of a chemically uniform substance, and therefore Guthrie,<sup>1</sup> who was the first to study these phenomena, supposed that the salt freezing out was a hydrate of the formula  $\text{NaCl} + 9\text{H}_2\text{O}$ . An investigation of this body shows that it consists of small crystals of ice mixed with crystals of salt, so that evidently the hydrate  $\text{NaCl} + 9\text{H}_2\text{O}$  does not exist. We may, *à priori*, deduce that on freezing a salt solution there must finally separate a mixture of ice and salt in constant proportions, but we are not entitled *à priori* to conclude that a hydrate of this composition exists, either in the solid or liquid state.

A phenomenon very like that just described occurs on heating a mixture of water and hydrochloric acid. Pure water

<sup>1</sup> Guthrie, *Phil. Mag.* (4), 1875, **49**, 1; (5), 1876, **1**, 49; **2**, 211; (5), 1884, **17**, 482.

boils at  $100^{\circ}$ , and pure hydrochloric acid at about  $-80^{\circ}$  under a pressure of 76 cm. The simplest case would be for the boiling-point to rise continuously as the proportion of water increases, just as is the case for mixtures of alcohol (B.Pt.  $78.2^{\circ}$  at 76 cm. pressure) and water (B.Pt.  $100^{\circ}$ ). If we distil such a mixture, we always find that the boiling-point of the residue rises. The law governing this phenomenon was enunciated by Gibbs<sup>1</sup> and Konowalow,<sup>2</sup> and may be deduced thermodynamically, as Gibbs has shown. The experimental facts corresponding to this law are so familiar to every chemist, that you will, no doubt, take the law for granted without my giving the rather abstract deduction of it from the laws of thermodynamics. On distilling a mixture of alcohol and water, the residue will always become less volatile—that is, its concentration with respect to water will increase. Therefore the distillate will contain a greater proportion of alcohol than the residue. This goes on until we have pure water remaining, after which the distillate is of the same composition as the residue, and the boiling-point remains constant. On this property depends the possibility of partially separating alcohol from its aqueous solutions, and of purifying it more and more by repeated distillation.

If we replace the ethyl alcohol by hydrochloric acid, the conditions are altered a little, because the boiling-point of solutions of this acid in water does not rise continuously as the proportion of water increases. Instead of this, the boiling-point (see Fig. 4) reaches a maximum at  $110^{\circ}$  C., when the composition of the solution is 20·24% (point *e*) of hydrochloric acid (at a pressure of 76 cm.). Therefore, if we distil a solution of this acid containing a greater percentage of hydrochloric acid (say 40%, point *a*), the boiling-point of the residue must become higher—that is, the residue must always become less rich in regard to hydrochloric acid as the distillation proceeds. In the diagram we move along the curve *ac*. This goes on till we have reached the maximum boiling-point ( $110^{\circ}$  C.) at *e*, after which it cannot but remain constant, and consequently the residue, as well as the distillate, must have a

<sup>1</sup> Cf. Gibbs, *Trans. of the Connecticut Acad.*, 3, 1876–1878.

<sup>2</sup> Konowalow, *Ann. Physik. u. Chemie.*, (3), 1881, **14**, 34 and 219.

constant composition (corresponding to 20·24% of hydrochloric acid).

We have an analogous case if we start with an acid containing less than 20·24 HCl, say 10% (point *b*). Here also the boiling-point must increase on continued distillation, according to the general law. The residue must therefore become continually richer in hydrochloric acid. This time we proceed in the diagram from the point *b* to the point *c*. If we distil a solution of hydrochloric acid at 76 cm. pressure, we obtain as end-product, both in the distillate and in the residue, an acid of the composition 20·24% HCl. This corresponds

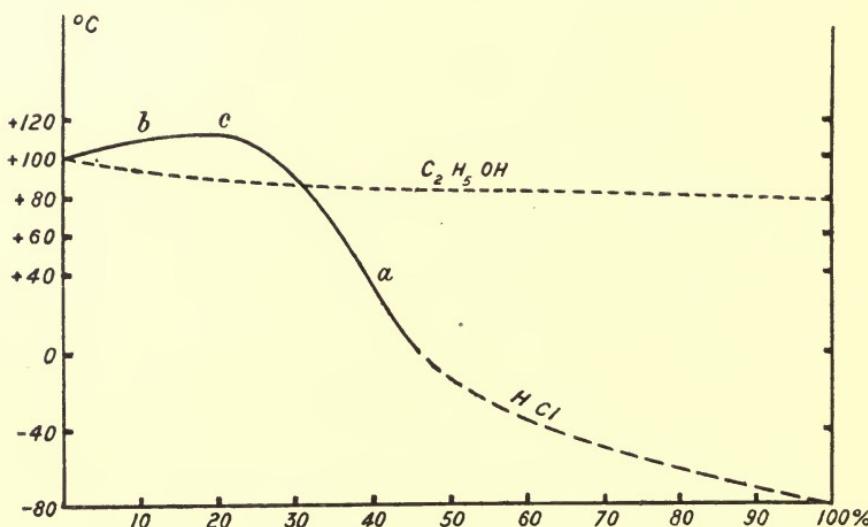


FIG. 4.—Boiling-points of solutions of ethyl alcohol and hydrochloric acid.

approximately to a composition represented by the formula  $\text{HCl} + 8\text{H}_2\text{O}$ . Now, it is a general method for the separation of different chemical individuals from one another to distil their mixture, and this operation succeeds in most cases, because they are analogous to the case of alcohol and water (dotted curve in the diagram), where no maximum boiling-point occurs at some definite concentration of the solution.

Chemists were so familiar with this method of purifying chemical compounds, that they were led to suppose that in this case, as in most others, the constant boiling-point indicated a chemical individual. They were, therefore, inclined to admit

that molecules of the formula  $\text{HCl} + 8\text{H}_2\text{O}$  exist. That this view is not correct has been shown by Roscoe,<sup>1</sup> who distilled solutions of hydrochloric acid at different pressures, namely, 5, 70, 80, and 180 cm. The composition of the solutions of maximum boiling-point, distilling at these pressures, was found to be different from that characteristic of a pressure of 76 cm.; instead of 20·24%, 23·2, 20·4, 20·2, and 18·2 respectively were the percentages found. Now, it follows from Dalton's law that a chemical individual must have the same composition under different circumstances; for instance, the water which we distil from aqueous solutions of alcohol has always the same properties, the pressure at which it is distilled being whatever we choose. Hence Roscoe concluded that the maximum boiling-point of solutions of hydrochloric acid does not prove that a hydrate corresponding to the formula  $\text{HCl} + 8\text{H}_2\text{O}$  exists.

There is another method of controlling this conclusion. We may separate mixed bodies from one another, not only by distillation, but also by shaking up with a third substance, for instance benzene, or by freezing the mixture. The latter method is the one applicable in this case. If we freeze a weak solution of hydrochloric acid, the process is nearly the same as that of freezing a weak solution of sodium chloride. Water separates from the solution in the form of ice, and the strength of the solution therefore increases. This goes on continuously, and we reach a point where the composition of the acid solution corresponds to the formula  $\text{HCl} + 8\text{H}_2\text{O}$ . If molecules of this composition were stable, we might expect that they would separate from the liquid on further cooling, so that its composition would remain constant, just as in the distillation. This is not the case, however; water freezes out, and the strength of the solution increases until we reach a point where a cryohydrate separates. A solution of which the composition is  $\text{HCl} + 2\text{H}_2\text{O}$  behaves in quite another way. This compound freezes out, on cooling at the constant temperature of  $-22^\circ$ , in the form of fine needles, and we therefore say that it is a real chemical individual (when in the solid, but not in the liquid state).

<sup>1</sup> Roscoe and Dittmar, *Journ. Chem. Soc.*, 1860, **12**, 128; also Roscoe, *Journ. Chem. Soc.*, 1860, **13**, 146.

Before leaving this subject it would be well to examine how a mixture of two components behaves, if there is a minimum boiling-point for a certain composition of the mixture. This occurs for solutions of propyl alcohol in water, the boiling-points of which are represented by the diagram (Fig. 5). If we examine the curve corresponding to a pressure of 76 cm., we find that pure water boils at 100° C., and pure propyl alcohol at 98° C. An admixture of the one of these substances with the other lowers the boiling-point, so that for a certain composition (about 70 % of alcohol), there occurs a minimum boiling-point

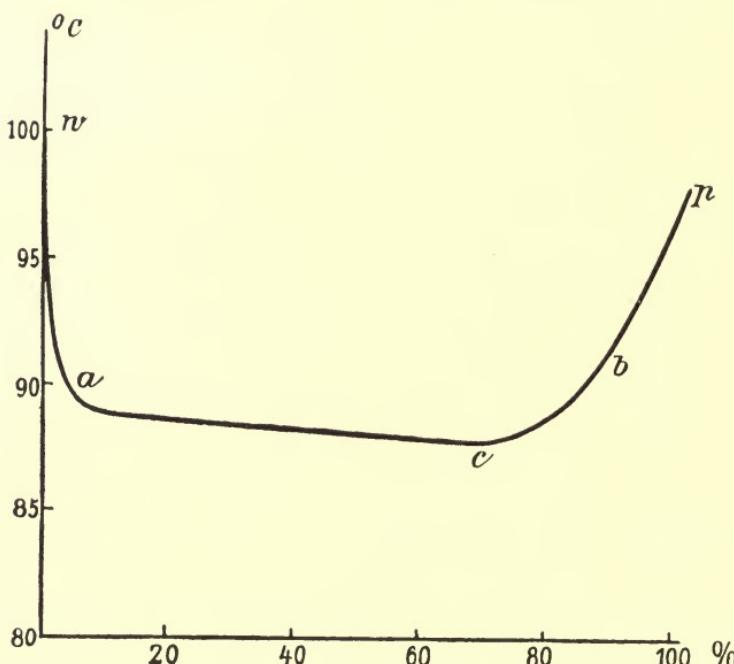


FIG. 5.—Boiling-points of solutions of propyl alcohol (Konowalow).

(87° C.). If we now take a solution which contains less propyl alcohol, say 5 % (point *a*), and distil it, the boiling-point will rise according to the general law, moving along the curve from *a* towards *w*—that is, the residue will become richer in water than the original solution was, and the distillate richer in propyl alcohol. In the same way, we find that if we begin with a solution containing more than 70 % of propyl alcohol (the point *b*), the residue on distilling will get richer in alcohol, and the boiling-point moves along the branch *bp* of

the curve. The distillate is more volatile than the mixture being distilled, and therefore contains less alcohol. We see that in this case we may approximate to a distillate of the constant composition of 70% propyl alcohol by successive distillations. Here, as in the case of hydrochloric acid, we cannot conclude that this solution corresponds to a definite hydrate. The composition of the solution with minimum boiling-point again changes with the pressure, so that at low pressures it is poorer in alcohol than at high pressures.

Many other substances, especially the hydrogen compounds of bromine, iodine, and fluorine, also nitric and formic acids, behave in the same manner as hydrochloric acid. In no one of these cases has it been possible to isolate hydrates by distillation.

As will be seen from all these examples, it is necessary to exercise much judgment in seeking for the existence of hydrates or other combinations in solutions. The most certain method to use is that of Jones, who dissolved both the substances examined, *e.g.* sulphuric acid and water, in a solvent fluid, and determined the number of molecules present by one of the methods of Raoult. Other methods which cannot be supported by theoretical considerations ought to be used very cautiously, otherwise we risk being led into wholly erroneous conclusions. The method of Jones has the disadvantage, that it only indicates the occurrence of compounds in the presence of a third substance, the solvent, in great excess. In all cases it is certain that the compounds which exist in presence of this solvent also exist in its absence. For the examination of the substances in the absence of a third substance as solvent, the conductivity method merits a higher degree of trustworthiness than other methods, because it has been better discussed.

It is to be regretted that most of the work done in connection with such researches has not been guided by clear theoretical considerations, and that consequently most of the conclusions so obtained have a very doubtful value. But the few researches on a solid theoretical basis—almost the only one which has given positive results is that on the compounds of sulphuric acid and water—seem to prove that hydrates occur in solutions as well as in the solid state. The hydrates with very great

molecular weights—as, for instance,  $\text{H}_2\text{SO}_4 + 150\text{H}_2\text{O}$ ,  $2\text{H}_2\text{SO}_4 + 25\text{H}_2\text{O}$ , or even  $\text{HCl} + 8\text{H}_2\text{O}$ —the existence of which had, from different physical properties, been inferred, seem not to exist in solution, at all events to any extent. It seems that in inorganic nature molecules built up of a very great number of atoms are not stable.

## CHAPTER IV

### *DISCUSSION OF THE VALIDITY OF DALTON'S LAW*

As we have already often had occasion to point out, the idea of the existence of many different kinds of atoms and their occurrence in combinations of definite proportions is wholly peculiar to chemistry. It seems much more natural to suppose that only one kind of primary matter exists, and one might suppose that this primary matter is the luminiferous ether which fills the whole of space, including the interstices between material molecules. Fresh attempts are always being made to imagine some mode of conversion of ether into matter, and *vice versa*. According to this view, that part of ether which we call matter should be different from the common imponderable ether which fills space. The simplest supposition seems to be that the motion is different in the two cases. Now, hydrodynamics teaches us that in a frictionless liquid there may exist vortices, and these vortices are wholly indestructible. The conception of such indestructible vortices seems to bear some analogy to the idea of indestructible atoms which we have constructed from our chemical experiences. Mathematical physicists have also endeavoured to find other properties of vortices which would be in agreement with our experimental knowledge of the properties of atoms, and this work has been partially crowned with success. But the great difficulty of working with this hypothesis is in strong contrast to the simplicity of the deductions from the atomic theory. Now, just as a theory is all the better the easier it is to use, as in the case of any other tool, so the conception of matter as consisting of ethereal vortices has found no marked acceptance among chemists. As far as I know, this idea has not led to the discovery of new

phenomena or new laws. On the other hand, it is very difficult to imagine anything in the nature of a frictionless fluid, as all fluids with which we deal are characterized by possessing viscosity. Furthermore, it is just as impossible to create vortices in a frictionless fluid as to destroy them; they must have existed from the beginning, and they would differ from common ether just as much as matter does. I am, therefore, of the opinion that it is more practical to keep to the simple atomic theory of Dalton than to substitute for it the academic hypothesis of ethereal vortices.

We have seen that in some operations, for instance, freezing or distilling a mixture, the portions separating from the liquid have the same composition as the liquid itself. Such mixtures are called hylotropic. If we imagine a hylotropic mixture which has the same composition after being submitted to different processes of separation, we should call such a mixture a chemical individual. For instance, water is a chemical individual, because we may distil it or freeze it, and it always retains the same properties as the original water, although we may have altered the circumstances, say the pressure, under which it was distilled or frozen. But if we heat the water to a very high temperature, say  $2000^{\circ}$  C., it is partially dissociated into oxygen and hydrogen (as Deville<sup>1</sup> proved). The same decomposition of water may be brought about by the aid of the electric current. Therefore we say that water is a chemical compound. Only such chemical individuals as have a constant composition under all external conditions would be called elements.

Recently a Bohemian chemist and natural philosopher, Franz Wald,<sup>2</sup> has expressed the opinion that the constant composition of chemical products depends on the manner in which they are produced.

He asserts that frequent attempts have been made to render the atomic hypothesis superfluous. "This circumstance might be quoted as a proof that this hypothesis is not capable of satisfying human thought. But all attempts in this direction, as far as I know, are characterized by an audacious flight

<sup>1</sup> Deville, *Compt. rend.*, 1857, **45**, 857; 1863, **56**, 195.

<sup>2</sup> Wald, *Zeit. physikal. Chem.*, 1895, **18**, 337; 1896, **19**, 607.

of thought, or, I might perhaps say, by a lack of thought. Difficulties do not exist for most writers on this subject; everything seems perfectly clear to them, but among their readers they find no credence."

Wald opens up a new way; he asserts that the chemist, without being conscious of it, prepares his substances so that they obey the laws of simple and multiple proportions. He meets the objection that Nature also produces chemical individuals by stating that chemically pure substances are very rare in Nature, and, further, that the processes by which Nature produces chemical individuals show an evident similarity to laboratory work.

In order to understand this statement better, we will briefly review the circumstances which determine the production of chemical substances in Nature.

The philosophers of antiquity had already observed the great difference between the three states of aggregation, gaseous, liquid, and solid, which are characteristic of natural products. The gaseous and the liquid states may be regarded as very nearly related to one another; it is possible to change a substance continuously from the liquid to the gaseous state, and *vice versa*. The common characteristic of both these states is the mobility of the particles of the substances concerned. If we have two gases, for instance, oxygen and hydrogen, in a flask, the lighter hydrogen above, we find that the two gases mix with each other by a process called diffusion, which finally gives a uniform mixture of hydrogen and oxygen in spite of the force of gravitation. To explain this phenomenon it seems necessary to suppose that the ultimate particles, the molecules, of both the gases are endowed with a ceaseless motion which causes them to intermingle completely with one another.<sup>1</sup>

The same is valid for two liquids which mix with each other in all proportions, for instance, alcohol and water. We therefore suppose an analogous motion of the particles of the liquids. Here, however, we come in contact with a new phenomenon, as it frequently happens that two liquids, for instance, ether and water, are not miscible in all proportions.

<sup>1</sup> We here neglect the extremely small influence of gravitation (or other external forces) upon these equilibria.

When we come to solid bodies, there is a vast difference. If we place a crystal of ice close to one of sodium chloride at a temperature below  $-21.3^{\circ}\text{C}$ ., the two do not mix with each other, but remain unchanged. On this peculiarity depends the property which was known even to the alchemists that usually only fluid, *i.e.* liquid and gaseous, but not solid bodies, react chemically. The molecules of solid substances differ from those of liquids by the peculiarity that they are fixed in a given position relatively to each other. They may possibly possess motion, but it consists only of oscillation about a mean position. There are some very remarkable exceptions to this rule. Some solid substances mix with each other, forming so-called "solid solutions," first characterized by van't Hoff.<sup>1</sup> For instance, gold diffuses into lead, although very slowly, at ordinary temperatures. At temperatures near the melting-point of the lead the process goes on much faster, as was shown by Roberts-Austen.<sup>2</sup> But the cases of "solid solution" are very rare, so that we may now neglect them. The property of liquids of dissolving foreign substances is closely connected with the mobility of their molecules and their relatively great density. This property is missing in the case of solid substances, with the exception of "solid solutions." Instead of the property of intermingling which we observe in molecules of liquid and gaseous substances, the molecules of solids show a tendency to collect together owing to the capillary forces. To illustrate the action of capillary forces, let us suppose that we have eight drops of water, each 0.01 millimetre in diameter, and one drop of double the diameter; the total volume would be the same in the two cases, but the surface would be twice as great in the first as in the second case. The capillary forces tend in general to diminish the superficial area of matter, therefore the second system is more stable than the first; also, if one of the eight drops were a little greater than the other seven, the latter would distil over to the former, as Lord Kelvin has shown. The same conclusion holds good for solid bodies, for instance, crystals surrounded by a solvent; therefore, large crystals grow at the expense of smaller ones. Volcanic rocks which have solidified rapidly, *e.g.* obsidian, possess a vitreous

<sup>1</sup> van't Hoff, *Zeit. physikal. Chem.*, 1890, 5, 322.

<sup>2</sup> Roberts-Austen, *Proc. Roy. Soc.*, 1900, 67, 100.

structure, their crystals not having had time to grow to sizes greater than the wave-lengths of light. On the other hand, igneous rocks which solidified slowly, such as granite, contain rather large crystals. Again, vitreous silicates, *e.g.* common window-glass, devitrify with time—that is, some of their sub-microscopic crystals grow larger. The crystals which have separated out from aqueous solutions are, in general, much greater than those from molten salts, especially from molten silicates. This peculiarity probably depends on the greater fluidity of aqueous solutions compared with that of molten substances.

Laboratory work uses this natural property of the capillary forces for preparing pure substances in solid form by crystallizing them out from their solutions. Chemists use repeated distillation for separating their products from one another, *e.g.* alcohol from water, only in cases where it is difficult to use crystallization owing to the low temperature required. It would be more true to say that laboratory work is similar to Nature's work rather than the converse, as Wald puts it.

Now, most substances, natural as well as artificial, occur in the solid state at ordinary temperatures, and these solid substances obey Dalton's law. But also when preparing gases we in most cases obtain pure (or nearly pure), substances, and therefore Dalton's laws hold good for them also; and indeed we saw that Dalton deduced his law mainly from observations on gases.

If the temperature were so high that no substances existed in the solid state, as is probably the case below a certain depth in the earth, it would be quite impossible to study chemistry, for then no vessels would exist for isolating chemical products. These would diffuse into one another and form some few phases containing inseparable mixtures of widely differing kinds of molecules. Chemistry is based upon the existence of solid substances which are characterized by their obeying Dalton's law, and therefore it is not right to assert that the acceptance of this law is based upon an arbitrary restriction.

We may now refer once more to the opinion of Wald. He says that we regard constant composition as a proof of chemical

<sup>1</sup> A good example for this case was the nitrogen prepared from air.

purity, and therefore purify substances until they show constant proportions. This may be true at the present time, but at the time when Berthollet had his controversy with Proust, or when Dalton discovered his law, it was not true. Taking as his starting-point the view, which was held at that time, that the constituents of chemical compounds are held together by forces which are analogous to the best investigated of all forces, namely, gravitation, Berthollet was led to the opinion that chemical compounds do not have a constant composition. Indeed, if a quantity of oxygen corresponds to the sun, and different quantities of hydrogen correspond to the planets, we may introduce just as many hydrogen planets as we wish; they will all be attracted by the oxygen sun. In other words, the system of sun and planets, which represents a quantity of water, might contain any desired proportion of hydrogen, or water should, according to this idea, not have a constant composition. It was only by actual experimental work that Proust was led to conclude that oxygen combines with tin in two perfectly definite proportions only, in contradiction to the prevailing ideas of that time, as represented by Berthollet. In the same manner Dalton, in his classical research on multiple proportions, investigated chemical compounds which occurred naturally at that time, or were prepared according to methods invented by chemists such as Cavendish, Priestley, Davy, and himself, without any preconceived ideas of their constant composition. It seems to me, therefore, that Wald's fundamental supposition, namely, that we acknowledge no substance as a simple chemical individual, unless it has a constant composition, was not tenable at the time when Dalton's law was formulated. Since the experimental evidence, accumulated during the century following, showed the correctness of this law, it seemed so well established that it could be used in the examination of the purity of chemical individuals. The fact that this application of the law has never led to false conclusions gives new and strong evidence in favour of its validity. Wald seems rather to be reasoning in a circle. Hence I think that the words of Helmholtz in his Faraday Lecture of 1881 are still valid: "We have not yet any theory sufficiently developed which can explain all the facts of chemistry as simply and

as consistently as the atomic theory developed in modern chemistry."

Attention has recently been called to the views of Wald, because Ostwald, in his Faraday Lecture, has supported them with the weight of his authority.<sup>1</sup>

Ostwald also attempts to deduce the law of multiple proportions and the law of combining weights from the law of constant proportions. If three elements, A, B, and C, form the compounds AB, AC, BC, and ABC, we first think of the compound AB being formed by A and B uniting together in definite proportions. The compound ABC can then be formed. In this Ostwald tacitly assumes that the constant proportions of the elements A and B remain unaltered; naturally this must first be proved. It seems to me, however, that one can just as validly assume that, if the quantity of A is taken as the unit, the quantity of B in AB is not even approximately the same as in ABC. The quantity of B which combines with the unit quantity of A is generally a function of the quantity of C contained in the compound. That this function assumes the simplest possible form, that of a constant, must be considered as a matter of experience, and not as *à priori* obvious. Similarly, the quantity of C which combines with the unit quantity of A is a function of the quantity of B in the compound.

Ostwald deduces the law of multiple proportions in a similar way, and the same objections may be made. The law of multiple proportions may be illustrated graphically as follows: The quantity of A which combines with different quantities of B and C is taken as the unit. The composition of the compounds  $AB_1$ ,  $AB_2$ ,  $AB_3$ , etc., is represented by equidistant points (distance apart =  $b$ ) on the B axis, i.e. the quantities of B combined with the unit quantity of A in different compounds stand to each other in simple rational proportions. (Some of these points may be missing if the corresponding compounds are not known.) In just the same way, the compounds of A and C may be represented by equidistant points (distance apart =  $c$ ) on the C axis.

All the compounds of A, B, and C can then be represented by points, the abscissæ and ordinates of which are simple

<sup>1</sup> Ostwald, Faraday Lecture, *Journ. Chem. Soc.*, 1904, **85**, 518.

multiples of  $b$  and  $c$  respectively. Now, the law of the constant composition of the compound ABC only demands that the ratio of the quantities of B and C which enter into combination shall be independent of the method of preparation of this compound. The point, however, which represents this compound graphically may have any position in the co-ordinate system BC, and no *a priori* conception can, in contradiction to

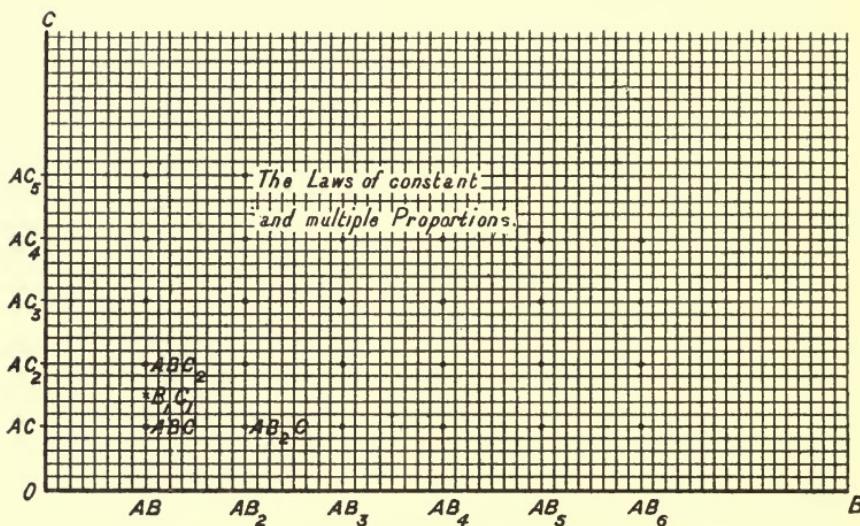


FIG. 6.

Ostwald's ideas, lead to the conclusion that it will be coincident with one of the aforementioned points. Similarly there is no *a priori* reason why the compound BC, which does not contain A, should be represented by the characteristic point of the compound ABC, so far as the ratio of the quantities of B and C in it are concerned. Rather can its composition, if B is fixed, be represented by any point  $B_1C_1$  under or above ABC.

## CHAPTER V

### *ELECTRICAL FORCES BETWEEN THE ATOMS— FARADAY'S LAW*

As we have already seen, it is impossible to suppose that the atoms in the molecule are held together by an attraction following the law of gravitation. The chemical attraction between the two kinds of atoms in a compound (considering the simple case of a compound of two kinds of atoms only) must in many cases, *e.g.* HCl, be of such a nature that as soon as the one kind of atom has united with the equivalent mass of the other kind, it exerts no further attraction on atoms of this second kind. In physics we have a similar case in the attraction between two electrically charged bodies. If we have a body, A, charged with the quantity  $a$  of positive electricity, it will attract negatively charged bodies, B, each one charged with the quantity  $b$ . Suppose one of these bodies, B, is brought so near to the body A that their charges come into close proximity; then the complex A + B will exert an attraction upon negative bodies as if it carried the positive charge  $a - b$ . It will attract and combine with more negative bodies, B, until a compound, A + nB, is formed which is electrically neutral, so that the charge  $a$  of A is equal to but of opposite sign from that  $nb$  of the nB bodies. As we know that chemical substances (which are not artificially electrified) are electrically neutral, we are led, according to this analogy, to the conclusion that every molecule contains one or more units of both positive and negative electricity, and that the number of positive electrical units connected with the positively charged atoms in a chemical compound is precisely equal to the number of negative electrical units bound to the negatively electrified

atoms in the same compound. For instance, we have every reason to suppose that the hydrogen atoms in the molecule of hydrochloric acid are positively charged. If we choose the charge of a hydrogen atom as the unit quantity, then the chlorine atom must be charged with the corresponding negative unit. We must, with Helmholtz and J. J. Thomson,<sup>1</sup> suppose an atomic constitution of electricity as well as of matter. But in electricity there are only two kinds of atoms, positive and negative, all of the same magnitude. We evolve in this way the supposition that the forces holding together the atoms in a molecule are very nearly related to electrical forces, an idea which has very often prevailed amongst chemists who were engaged in the investigation of electro-chemical problems. The development of this idea is of very great interest, and we now proceed to review its history.<sup>2</sup>

In the middle of the eighteenth century the striking effects produced by electrical machines were the object of much research. The physiological effects were the most startling, and were studied by the greater number of experimenters; but also nearly all the then known chemical products were submitted to the action of electricity, and occasionally valuable observations were made. Thus Beccaria found that oxides of metals are reduced, and he produced zinc and mercury in this way. A little later Priestley carried out his great work on the physics and chemistry of gases. He subjected air to the influence of electric sparks, and found that an acid was formed. He mistook it for carbonic acid, but it was recognized by Cavendish to be nitric acid. Priestley also passed electric sparks through oil and ether, and found that a gas containing hydrogen was evolved. Van Marum repeated the researches of Beccaria and Priestley on a larger scale. He found that the electric spark not only reduces metallic oxides, but that it also sometimes causes the oxidation of certain metals, *e.g.* lead, with the aid of the oxygen of the air. He also found that many liquids and solids, as, for instance, alcohol and camphor, give hydrogen under the influence of electric sparks. In his experiments,

<sup>1</sup> Cf. J. J. Thomson, "Electricity and Matter."

<sup>2</sup> This history is given in detail in Ostwald's "Elektrochemie, ihre Geschichte und Lehre" (Leipzig, 1896).

water gave hydrogen, but no oxygen; van Marum explained this as being due to the combination of the oxygen with mercury. Ammonia gave a mixture of nitrogen and hydrogen.

A little later (1789) Deimann and Paets van Troostwyk succeeded in decomposing water into oxygen and hydrogen. They employed a tube, closed at the top, and with a metal wire sealed in. This was connected with one pole of a large frictional machine, the other pole being connected with a wire introduced through the open lower end of the tube. The tube was filled with water and stood in a basin of water. The electric spark produced gas-bubbles in the water, which was driven down the tube as the gas collected, until the upper metal wire was no longer in contact with the water. The spark then passed through the gas, which in consequence exploded. It proved to be a mixture of oxygen and hydrogen. Probably the greater part of the gas evolved was due, as later experiments of Perrot<sup>1</sup> seem to show, to the thermal effect of the spark, and not to its electrolytic action.

Ritter repeated this experiment, using electrodes of silver wire and a solution of a silver salt instead of water. He found that a thin deposit of silver was deposited on the negative pole. On reversing the current this silver deposit was dissolved again. This experiment seems to be the first one clearly establishing the electrolytic action of the electric current.

In 1795, Volta arranged the metals in a series according to the electrical charges they assume on contact. Ritter showed that the same series is obtained if the metals are ranged according to their ability to displace one another from solutions of their salts.

The construction of the voltaic pile by Volta in 1800 gave a new character to electrical researches. The physiological effects and the size of the electric sparks produced by a pile were not nearly so startling as those obtained with the old electrical machine, but, on the other hand, the pile produced much greater chemical effects. The difference between the pile and the electrical machine is that the former gives a great quantity of electricity of low potential, whereas the opposite is true for the latter. Now, the chemical effects are only

<sup>1</sup> Perrot, *Compt. rend.*, 1858, **46**, 180; **47**, 359.

dependent on the quantity of electricity, and therefore the pile was most valuable for studying electrochemical phenomena.

The peculiar effects of the voltaic pile attracted general interest, so that much research was done with it very soon after its construction. Thus the classical work of Nicholson and Carlisle on the decomposition of water (containing dissolved salt) into hydrogen and oxygen was carried out as early as 1800. At first they used brass electrodes, and found that hydrogen was evolved at the electrode connected with the silver pole of the pile. (This was made of combinations of half-crown pieces and zinc plates, separated from one another by pieces of paste-board saturated with acidulated water. The silver pole was therefore the negative one.) The other brass electrode, connected with the positive zinc pole of the pile, was oxidized, no oxygen being set free. Afterwards they used platinum electrodes, and then they found that the oxygen formed at the positive pole was given off as a gas, although its quantity was not so great as that of the hydrogen evolved from the negative pole. They were very astonished at this result, as they had expected to find both oxygen and hydrogen liberated at each pole. They also observed that litmus turned red at the positive pole, and that chemical processes were going on in the pile itself while it was producing electricity.

Davy also made experiments with the voltaic pile, and was early (1801) led by them to suppose that the chemical processes going on in the pile were the true cause of the electric current, and not the contact of the metals, as Volta supposed. He constructed piles with only one metal, copper, and two liquids, a solution of nitric acid and a solution of sulphide of potassium, and in this way proved the correctness of his views. At that time it was supposed that water was decomposed into acid and alkali. Davy showed this supposition not to be borne out if pure water was used in a gold vessel. The observation depended on the use of vessels of glass or other materials, which were partially dissolved by the water. A few years later Davy prepared for the first time the alkali metals, sodium and potassium, by decomposing caustic soda and caustic potash with the help of the electric current. These researches were extended later on by Bunsen and his pupils.

The brilliant discoveries and wide-reaching researches of Davy led him to the idea that chemical affinity is caused by the electrical charges on the atoms, which thus attract one another. Making use of Volta's idea, that two bodies become charged with opposite kinds of electricity when they are brought into contact, Davy supposed that contact action was the source of the electrical charges on the atoms. On electrolysis the atoms are attracted to the pole of opposite sign to that of their own electric charge. By the electrolytic process the atoms are brought back to the uncharged state which characterized them before their union.

About the same time (1807) Berzelius published the electro chemical researches carried out by himself and Baron Hisinger. They drew the following conclusions from their experiments:—

Neutral salts are decomposed by the electric current. In general chemical compounds are decomposed by the current, and their components collect at the poles.

To the negative pole migrate combustible substances (*e.g.* hydrogen), alkalis, and earths; to the positive pole, oxygen, acids, and oxidized compounds. The same substance may in some cases migrate to the positive, in other cases to the negative, pole. Thus, for instance, nitrogen wanders to the negative pole during the electrolysis of ammonia, and to the positive pole, together with oxygen, on the electrolysis of nitric acid. This point was of importance for the electro-chemical views of Berzelius, according to which the same atom might sometimes behave as a positively, sometimes as a negatively, charged body, it depending upon the other atom or atoms with which it was combined.

Since all compounds of oxygen evolve this gas at the positive pole, oxygen was regarded by Berzelius as the most negative of all substances. Next to it came sulphur, selenium, nitrogen, the halogens, phosphorus, etc., which only went to the negative pole when they were liberated from their compounds with oxygen, but otherwise to the positive pole. With oxygen these negative substances form very strong acids, which likewise wander to the positive pole. For this reason he placed other substances which give acids with oxygen near to the oxygen

end of his series, and the stronger the acid was the nearer the substance in question was placed to oxygen.

In the same manner Berzelius showed potassium to be the most positive of all elements. Next to it were placed the other alkali metals, and then the metals of the alkaline earths. These metals are known to displace all other metals from aqueous solutions of their salts. The other metals were therefore arranged so that that metal which replaced another from its salt was placed nearer to potassium. Ritter had already shown that the order of metals obtained in this way is the same as that in Volta's series, which was arranged according to the electrical charges the metals assumed on contact with each other; the Berzelius series of elements on the positive side thus coincided with Volta's series.

From the series of Berzelius one could deduce, according to him, that in the electrolysis of a compound the element which is nearer to oxygen in the series will be deposited at the positive pole, while the other element which is farther removed from oxygen, and therefore more positive, will be deposited at the negative pole. His series of elements is as follows:—

Oxygen	Boron	Palladium	Thorium
Sulphur	Carbon	Silver	Zirconium
Selenium	Antimony	Copper	Aluminium
Nitrogen	Tellurium	Uranium	Yttrium
Fluorine	Tantalum	Bismuth	Beryllium
Chlorine	Titanium	Tin	Magnesium
Bromine	Silicon	Lead	Calcium
Iodine	Hydrogen	Cadmium	Strontium
Phosphorus	Gold	Cobalt	Barium
Arsenic	Osmium	Nickel	Lithium
Chromium	Iridium	Iron	Sodium
Vanadium	Platinum	Zinc	Potassium
Molybdenum	Mercury	Manganese	
Tungsten	Rhodium	Cerium	

Berzelius' own idea of the cause of the electric charge on the atoms was very hazy. He was of the opinion that the atoms were already electrified before coming into contact. Each atom might carry simultaneously positive as well as negative

electricity. The charges were imagined to be concentrated around two poles. According as the action of the positive or negative pole preponderates, the atom shows positive or negative properties—that is, it is attracted by the negative or positive pole of the voltaic pile.

Ampère, in 1821, expressed the opinion that the atoms possess a certain invariable charge of electricity, *e.g.* potassium a positive one. As long as the atom was free, an equal charge but of opposite sign was attracted to its surface from the surrounding medium, so that the whole was in this manner electrically neutral. If a negative and a positive atom came into contact, their charges did not need to attract any more electricity from the surrounding medium, but they combined with each other, and the surrounding charge disappeared.

The ideas on this subject were not clear until Faraday, in 1834, discovered his law, that in the electrolysis of different

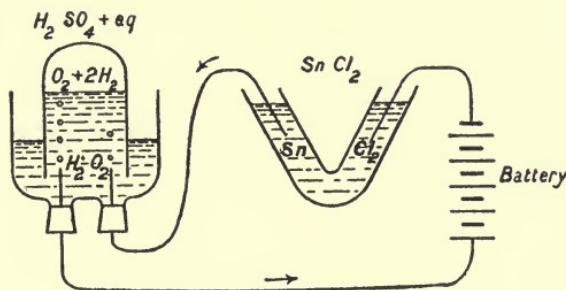


FIG. 7.

chemical compounds equivalent quantities of the different products appearing at the electrodes—these products were called ions—were set free by the same quantity of electricity. To prove his law, he passed the same quantity of electricity through two vessels arranged in series, as shown in Fig. 7. When the current had been passing for a certain time, the quantities of ionic products in both the vessels were measured. For instance, the one vessel contained stannous chloride, kept molten by means of a spirit-lamp, and the other was a voltameter containing acidulated water. He found that 3·2 grains of tin were deposited, and 3·85 cubic inches of oxyhydrogen gas were evolved in the voltameter, corresponding to 0·497 grain. Since the equivalent weight of water (or oxyhydrogen gas) is 9 (9

times that of hydrogen, which was used as unit), the equivalent weight of tin, calculated according to Faraday's law, is  $\frac{32}{0.497} \times 9 = 57.9$ . At Faraday's time this equivalent was given as 58; modern determinations give 59.4 (atomic weight of Sn = 118.8).

In the same way Faraday determined the so-called electrochemical equivalents of different substances (that is, the quantities which are liberated by the same amount of electricity as that required to liberate the unit weight of hydrogen), and he found that the electro-chemical equivalents correspond completely with the chemical equivalents.

It is very astonishing to find that Faraday, as can be seen from his writings, nevertheless supposed that a current, if weak enough, may pass through an electrolyte without decomposing it. As a matter of fact, the decomposition is not always visible when very weak currents are used, because the products of decomposition, *e.g.* oxygen and hydrogen, are dissolved by the surrounding liquid. By this supposition he contradicted his own law. Berzelius opposed it very strongly; he held the opinion that the most stable compounds are held together by the strongest charges.

During the electrolysis of water, for example, it seemed most startling that both its constituents did not appear at the same place (as Nicholson and Carlisle had expected), but at some distance from each other, namely, at the two electrodes, which may be placed at any desired distance apart. We must, therefore, not be surprised that Ritter put forward the idea that hydrogen is a compound of water and negative electricity, and oxygen a compound of water and positive electricity. But this idea was not in accordance with Lavoisier's proof that water is a compound of hydrogen and oxygen only, and therefore Grotthuss formulated the following hypothesis, which was generally accepted to explain the conduction of electricity through electrolytes. He supposed that, under the influence of the electric charges on the two electrodes, the molecules of the electrolyte, for instance, of potassium chloride, arrange themselves so that they all turn their positive part, the potassium atom, towards the negative electrode (see Fig. 8). The molecules

are arranged in a manner analogous to the supposed arrangement of the small molecular magnets in a magnet. Electrolysis consists of liberating the outermost potassium atom at the negative electrode, and the outermost chlorine atom at the positive electrode. Grotthuss, as well as Davy and Faraday, regarded the electrodes as the paths ("electrode" was derived by Faraday from a Greek word signifying "path of electricity") by which the positive and negative electricities entered the electrolyte to combine with the negative and positive ions.

After the first ions are deposited, the chlorine atom of the first molecule combines with the potassium of the second molecule, the chlorine atom of this latter molecule with the potassium atom of the third molecule, and so on (Fig. 8, b).

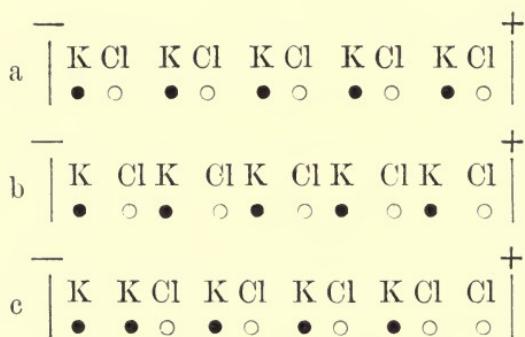


FIG. 8.

Under the influence of the charges of the electrodes these turn round again, so that they become "polarized" (Fig. 8, c). Electrolysis then commences afresh, liberating the second potassium atom and the last but one chlorine atom, and so on. This wandering of the positive and negative parts of the molecule, which we now call ions, does not go on with the same velocity for different ions. This was shown by Hittorf in his masterly work on the migration of ions, carried out in the middle of last century. To this research, which is intimately connected with the dissociation theory of electrolytes, we shall refer again later on. In order to avoid unnecessary difficulties, we anticipate here the results of this theory. According to it, the conducting molecules are split up into their charged ions, which move about freely in the electrolytic liquid. If we now dip

two electrodes which are connected with an accumulator into this liquid, the latter receives a higher electrical potential at the positive electrode than at the negative one. All positively charged substances, and therefore the positive ions, move, if they are free, from higher to lower potentials, and negatively charged bodies, including negative ions, in the opposite direction. The velocity of the ions depends only on the rate of the fall of potential, and on the friction of the ions against the surrounding liquid. This friction is not the same for all ions, and therefore they move with different velocities under the influence of the same electrical force.

The meaning of Faraday's law, according to these modern conceptions, is very simple. Suppose we have a very dilute solution of hydrochloric acid, in which we dissolve sodium. The HCl molecules are (practically) completely dissociated into their ions—hydrogen ions, which are charged positively, as they wander with the current from higher to lower potential, and chlorine ions, charged just as strongly negatively, since the liquid is electrically neutral. Here the composition of the molecule is so simple that there cannot be any doubt as to the composition of the ions. The contact of the acid with electrically neutral sodium brings about solution of the latter, and a chemically equivalent quantity of electrically neutral hydrogen gas escapes. The hydrogen atoms, when they existed as ions, were positively charged, and since they now escape in the neutral state, they must have given up their whole charge to the liquid. This charge must have gone to the dissolved sodium, for the other parts of the liquid are unchanged. Therefore the sodium ions in the new solution carry just as much positive electricity as the chemically equivalent quantity of hydrogen ions did before. This is one way of expressing Faraday's law. In exactly the same way as above, we can prove that if a positive ion is replaced by another—whereby necessarily equivalent quantities are exchanged—this new ion carries just as big a charge as the old one. This charge is found to be 96,500 coulombs for one gram of hydrogen. Since, now, in sodium chloride the positive ion is sodium, all substances which can replace sodium chemically in sodium chloride play the *rôle* of positive ions. These are the various metals, together

with hydrogen, ammonium, uranyl ( $\text{UO}_2$ ), and many other so-called compound radicles mostly belonging to organic chemistry. The negative ions are the residues of the salts or acids when they are deprived of their metals or hydrogen atoms respectively. Thus, for instance, the ions of potassium ferrocyanide,  $\text{K}_4\text{FeC}_6\text{N}_6$ , are  $4\text{K}$  and  $\text{FeC}_6\text{N}_6^-$ , the latter carrying four atomic charges, because it is equivalent to four  $\text{K}$  ions, each of which carries one atomic charge. The ions of phenylammonium chloride,  $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ , are  $\text{C}_6\text{H}_5\text{NH}_3^+$  (because it may be regarded as replacing  $\text{K}$  in  $\text{KCl}$ ) and  $\text{Cl}^-$ , each carrying one atomic charge.

If zinc is substituted for hydrogen in hydrochloric acid, every atom of zinc replaces two atoms of hydrogen; therefore we say that the zinc ion carries two atomic charges of electricity. This evidently corresponds to the chemical expression that zinc is a divalent body. In the same manner we find that the aluminium ion carries three atomic charges, which signifies that it is chemically trivalent. Some metals give two different ions; for instance, iron, the ions of which are divalent in the ferrous compounds, and trivalent in the ferric compounds. Sometimes a metal gives two ions of different composition, but having the same valency; *e.g.* mercury gives the divalent ions  $\text{Hg}_2$  in mercurous, and  $\text{Hg}^+$  in mercuric compounds.

## CHAPTER VI

### *ELECTRICAL FORCES BETWEEN THE ATOMS (CONTINUED): CHEMICAL VALENCY AND AFFINITY*

EVIDENTLY we here come into close touch with the difficult rules of valency. As long as we consider ordinary electrolytes the case is extremely simple. But if we draw the obvious conclusions from the statement that all the atomic complexes which may replace a metal in one of its salts, or which may be replaced by a metal, also play the rôle of ions in their compounds, we are led to a system corresponding closely to Berzelius' so-called dualistic system of chemistry, and which has to contend with very important difficulties.

This step was taken by Helmholtz in his renowned Faraday Lecture of 1881,<sup>1</sup> which, so to say, revived the theory of Berzelius, which had been abandoned some forty years before, because of the victorious attacks upon it connected with the development of modern organic chemistry. Dumas had, for instance, found that chlorine, which (according to Berzelius) was a very strongly negative element, could replace the positive element hydrogen in acetic acid, and the substitution product had very nearly the same properties as the original acetic acid. This fact seemed inexplicable by the Berzelius theory, and on this and similar grounds the theory was given up. (Berzelius might have made use of his statement, that the same atom may sometimes be positive and sometimes negative, as he had, for instance, supposed in the case of nitrogen.) Helmholtz recalls that Faraday already had expressed the opinion that sulphur is negatively charged in silver sulphide, but positively in strong sulphuric

<sup>1</sup> Helmholtz, Faraday Lecture, *Journ. Chem. Soc.*, 1881, 39, 277.

acid. "Afterwards he (Faraday) suspected that the deposition of sulphur from sulphuric acid might be a secondary result. On electrolyzing strong sulphuric acid, the cathion (positive ion) may be hydrogen, which combines with the oxygen of the acid and drives out the sulphur. But if this is the case, hydrogen, recombined with oxygen to form water, must retain its positive charge, and it is the sulphur which in our case must give up positive charges to the negative electrode. Therefore this sulphur of sulphuric acid must be charged with positive equivalents of electricity. The same reasoning may be applied in a great many other instances." "Now arises the question, Are all these relations between electricity and chemical combination limited to that class of bodies which we know as electrolytes?" Helmholtz gives two delicate methods of detecting electrolytic conduction. The one consists in the observation of the so-called electrolytic polarisation after the passage of a current through an electrolytic conductor. If we dip two platinum plates into an electrolyte and connect them for a time with a galvanic battery, and afterwards replace the battery by a quadrant electrometer, the two platinum plates then show a potential difference. This depends on a change in the nature of the platinum plates; they are coated with thin layers of the two decomposition products liberated from the electrolyte during the electrolysis. A pupil of Helmholtz, Picker, carried out such experiments, using a battery of eight Daniell cells, which he allowed to act upon the supposed electrolyte for twenty-four hours. He observed deflections of the electrometer, corresponding to about 0.35 volt for the purest alcohol, ether, and oil of turpentine, and about 0.9 volt for benzene.

The other method consisted in placing two different metal plates in contact with the substance under examination, and testing them for a potential difference. "If the connection lasts long enough, even glass, resin, shellac, paraffin, sulphur—the best insulators we know—give the same effect as electrolytes."

"All these facts show that electrolytic conduction is not at all limited to solutions of acids (bases) or salts. It will, however, be a rather difficult problem to find out to what extent

electrolytic conduction exists, and I am not yet prepared to give a positive answer."

Later on, Helmholtz seems to incline to the idea that all chemical compounds are electrolytes. "If we conclude from the facts that every unit of affinity is charged with one equivalent either of positive or of negative electricity, they can form compounds, being electrically neutral, only if every unit charged positively unites under the influence of a mighty electric attraction with another unit charged negatively. You see that this ought to produce compounds in which every unit of affinity of every atom is connected with one, and only one, other unit of another atom. This, as you will see immediately, is the modern chemical theory of quantivalence, comprising all the saturated compounds. The fact that even elementary substances, with few exceptions, have molecules composed of two atoms, makes it probable that even in these cases electric neutralization is produced by the combination of two atoms, each charged with its full electrical equivalent, not by neutralization of every single unit of affinity."

"Unsaturated compounds with an even number of unconnected units of affinity, offer no objection to such an hypothesis; they may be charged with equal equivalents of opposite electricity. Unsaturated compounds with one unconnected unit, existing only at high temperatures, may be explained as dissociated by intense molecular motion of heat in spite of their electric attractions. But there remains one single instance of a compound which, according to the law of Avogadro, must be considered as unsaturated even at the lowest temperatures, namely, nitric oxide (NO), a substance offering very uncommon peculiarities, the behaviour of which will be perhaps explained by future researches."

These words give a very clear idea of the opinions prevalent among chemists at that time. Helmholtz was not familiar enough with chemical phenomena to try to modify them. He could even then have named another substance, namely  $\text{NO}_2$ , which did not conform to the rules of valency accepted in his time. Since then the measurements of vapour-densities, as well as of freezing-points, have indicated the existence of molecules, the composition of which, determined according to

the laws of Avogadro and van't Hoff, agrees no better with the old rules of valency than the molecular formula NO does.

Chemists, therefore, have given up the old idea that unsaturated compounds always show an "even number of unconnected units of affinity." At the present time most of them seem to incline to the opinion that nitrogen may be 1-, 2-, 3-, 4-, or 5-valent in its compounds with oxygen, and that other elements may possess varying valency. In most cases, it is true, the valency changes by even numbers, but not always.

During the electrolysis of a compound, for instance water, electrical work is done in overcoming all the forces which hold the constituent parts of the molecules together. It is very easy to calculate this work; it is the product of the quantity of electricity necessary for the decomposition and of the electromotive force. If the quantity of electricity is measured in coulombs, and the electromotive force in volts, we get the work expressed in joules (1 joule = 0·24 calorie).

Now, according to Faraday's law, for the electrolysis of one gram-equivalent of a compound, the same quantity of electricity, namely 96,500 coulombs, is always necessary. Therefore, if we call the electromotive force used in the decomposition  $e$ , the work done in electrolysing a gram-equivalent is—

$$A = 96,500e \text{ joules} = 23,070e \text{ calories}$$

This work necessary for the decomposition is proportional to the electromotive force, and therefore this magnitude may be regarded as a measure of the affinity holding the molecules together. The study of electromotive forces is responsible to a great extent for clearing up our ideas of chemical affinity, and it has also shown that this magnitude is not proportional to the heat developed in the formation of molecules from their components. For instance, the electromotive force necessary to decompose water, using palladium electrodes, which absorb the decomposition products H<sub>2</sub> and O<sub>2</sub>, is found to be about 1·1 volt. The work done in electrolysing one gram-equivalent is therefore  $1\cdot1 \times 23,370 = 25,377$  calories. The heat of combustion of one gram-equivalent of hydrogen (1 gram) is 34,200 calories, totally different from the work done in overcoming the affinities.

The forces holding together the molecules may be of

different kinds. Berzelius, Davy, and Faraday were of the opinion that the chief force is the attraction between the electric charges on the atoms, and this Helmholtz showed to be very probable by the following considerations: 1 coulomb is equal to  $3 \times 10^9$  electrostatic units. The charge on one gram of hydrogen is 96,500 coulombs =  $28,950 \times 10^{10}$  electrostatic units.

The electrostatic unit of electricity is so defined that two small particles, both charged with such a unit of positive electricity, repel each other with a force of 1 dyne, if they are 1 cm. distant from each other. If the one of them were positively, the other negatively, charged with this unit charge, they would attract each other with a force of 1 dyne. This attraction is inversely proportional to the square of their distance apart, so that two such particles placed at a distance of 1 km. (=  $10^5$  cm.) would attract each other with a force of  $10^{-10}$  dynes, or, since a dyne is equal to  $1.02 \times 10^{-6}$  kgm., with a force of  $1.02 \times 10^{-16}$  kgm. weight. Further, the attraction is proportional to the charges on both the particles, so that if these were charged with the quantity of electricity carried by one gram of hydrogen, their attraction at a kilometer distance would be  $28,950 \times 10^{10} \times 28,950 \times 10^{10} \times 1.02 \times 10^{-16} = 8.54 \times 10^{12}$  kgm.

We may compare this attraction with that exerted by gravitation. The gravitation-constant is  $6.67 \times 10^{-8}$ ; in other words, two masses each of 1 grm. attract each other with a force of  $6.67 \times 10^{-8}$  dynes, if they are placed at a distance of 1 cm. from each other. From this we may easily calculate that two similar masses which, placed 1 km. apart, attract each other with the force of  $8.54 \times 10^{12}$  kgm. would each have a mass of  $1.12 \times 10^{18}$  grm. =  $1.12 \times 10^{15}$  kgm. As the mass of the earth is  $5.985 \times 10^{24}$  kgm., the mass of these attracting bodies would be  $5.34 \times 10^9$  times less than that of the earth; *i.e.* if they were made of the same material as the earth (sp. gr. 5.52) their radii would be 1750 times less than that of the earth, that is, 3.65 km. From this it is apparent how much greater are the electrical attractions between the atoms than the gravitational forces.

We may now make a calculation of the energy necessary to

tear asunder the atoms of a molecule, for instance, a molecule of water. One gram of hydrogen at 0° C. and 76 cm. pressure occupies 11,200 c.c., and the number of gas-molecules in 1 c.c. at 0° C. and 76 cm. pressure is calculated to be about  $21 \times 10^{18}$ . Therefore 1 grm. of hydrogen contains  $11,200 \times 21 \times 10^{18} = 2356 \times 10^{20}$  molecules, and double the number of atoms. The charge on one atom of hydrogen is therefore  $\frac{28950 \times 10^{10}}{2 \times 2356 \times 10^{20}}$   $= 6.14 \times 10^{-10}$  electrostatic units, and the charge on one atom of oxygen is double this. The work done when two small spheres, an infinite distance apart, and each charged with one electrostatic unit, are brought to a distance  $r$  cm. from each other, is equal to  $\frac{1}{r}$  erg  $= \frac{1}{418 \times 10^5 \times r}$  calories. Hence, if the one atom of oxygen and two atoms of hydrogen are brought from an infinite distance apart to a distance of one hundred millionth of a centimetre from each other (about the molecular distance in solids and liquids), the work done corresponds to—

$$(12.28 \times 10^{-10} \times 12.28 \times 10^{-10} - 6.14 \times 10^{-10} \times 6.14 \times 10^{-10}) \frac{10^8}{418 \times 10^5} \text{ cal.}$$

$$= 0.27 \times 10^{-17} \text{ cal.}$$

The first term is due to the attraction of the charge on the atom of oxygen upon the charges on both the hydrogen atoms, and the second term to the mutual repulsion of the charges on the two hydrogen atoms. Now, 1 grm. of hydrogen contains  $2356 \times 10^{20}$  molecules, and 9 grms. of water consist of just as many atoms of oxygen and double the number of atoms of hydrogen. The electrical work is therefore  $2356 \times 10^{20} \times 0.27 \times 10^{-17} = 636120$  calories.

This energy represents that necessary for the decomposition of a molecule of water into its constituent atoms, if these are held together only by electrical forces. It is 18.6 times as great as the heat developed (34,200 cals.) by the formation of 9 grms. of water from hydrogen and oxygen in the gaseous state. But there is a great difference between these two magnitudes. The decomposition of two molecules of water may be considered to take place in two stages: (1) separation of the two water-molecules into two molecules of hydrogen and one molecule of oxygen; and (2) the decomposition of these hydrogen and

oxygen molecules into their respective atoms. It is very reasonable to suppose that the latter work is 17·6 times as great as the former. We conclude, therefore, that the electrical forces holding together atoms in molecules are of such a magnitude that we need not look for other forces for this purpose, and it is also probable that these electrical forces are the only, or at least the chief, forces which bind the atoms together.

This conclusion, which was stated by Helmholtz in his Faraday Lecture, is strongly supported by the calculations of Richarz<sup>1</sup> and Ebert,<sup>2</sup> which are based on the heats of dissociation of nitrogen peroxide ( $N_2O_4$ ), iodine, and hydrogen. The calculations are similar to those given above.

The mistake made by Berzelius consisted in supposing that the forces with which a valency acts are dependent only on the magnitude of the electric charge. According to the law of Faraday, the electrical quantities for each unit of valency are always the same, but, nevertheless, the combining force may be of a very different strength, depending on the distance apart of the electric charges. The work necessary to decompose such a combination is twice as great if the charges lie half the distance apart as when they are separated by the unit distance.

We have already seen how the work necessary for splitting up a compound, in this case water, can be calculated from the electromotive force required to decompose it. One must thereby take care that the process is reversible, *i.e.* that the same amount of work can be obtained again if the process is carried out in the reverse direction. For example, in the decomposition of water (with addition of acid or alkali) between platinum electrodes, Leblanc<sup>3</sup> found that an electromotive force of about 1·67 volts was necessary, *i.e.* about one and a half times as great as that given above for the decomposition between palladium electrodes. As a matter of fact, the decomposition between platinum electrodes is not reversible. However, another fact could be deduced from Leblanc's experiment,

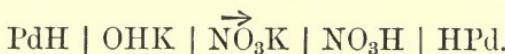
<sup>1</sup> Richarz, *Sitzungsber. d. Münchener Akad. d. Wiss.*, 1894, **24**, 1.

<sup>2</sup> Ebert, *Ann. Physik. u. Chem.* (3), 1895, **56**, 255; (4), 1903, **12**, 714.  
Cf. also Becker, *Ann. Physik.* (4), 1905, **17**, 8.

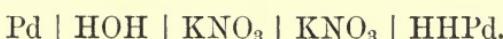
<sup>3</sup> Leblanc, *Zeit. physikal. Chem.*, 1891, **8**, 299; 1892, **12**, 333.

namely, that the work necessary for the decomposition of water is independent of the nature of the added acid or base. It is thereby taken for granted that actually oxygen and hydrogen are deposited at the electrodes, which would not be the case, for instance, if the acid added were a halogen hydride.

The work necessary for the decomposition of a chemical compound very nearly corresponds to the old but less precise idea of affinity. By determining electromotive forces we are able to measure the affinities which are exerted in many chemical processes. For example, we can determine the affinity which comes into play when an acid, *e.g.* HNO<sub>3</sub>, is neutralized by a base, *e.g.* KOH. We build up a galvanic cell which is composed of the following parts:—

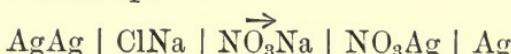


If a current is passed in the direction indicated by the arrow, *i.e.* from the palladium foil charged with hydrogen through the solutions of caustic potash, saltpetre, and nitric acid to the second piece of palladium foil charged with hydrogen, the composition after the passage of 96,500 coulombs is the following:—

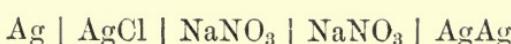


During the process, therefore, a gram-molecule each of KOH and HNO<sub>3</sub> is changed into H<sub>2</sub>O and KNO<sub>3</sub>. (In the migration of hydrogen from left to right, no work is done.) The electromotive force of this element is 0·675 volt, and the work done, expressed in calories, is therefore  $23,070 \times 0\cdot675 = 15,570$  cal. The observed evolution of heat in this process is somewhat less, namely, 13,550 cal.

In a similar manner the affinity can be determined, in consequence of which a difficultly soluble salt is precipitated out on mixing the solutions of two easily soluble salts, *e.g.* AgCl from a mixture of AgNO<sub>3</sub> and NaCl. A galvanic cell of the following composition is made up:—



When the current passes in the direction of the arrow, the combination becomes—



i.e. a change from NaCl and AgNO<sub>3</sub> into AgCl and NaNO<sub>3</sub> has taken place.

The most important interaction, the affinity of which can be measured in this way, is that which takes place when one metal replaces another from one of its salts, e.g. in the interaction between zinc and copper sulphate. This process takes place in a Daniell cell—



The electromotive force of this combination is about 1.1 volt, corresponding to 25,380 cal. This affinity corresponds very nearly to the heat evolved, 25,065 cal., when 1 gram-equivalent of zinc (32.7 grms. =  $\frac{1}{2}$  gram-atom) replaces copper from dilute solution. Now since, according to the views of thermochemists, the evolution of heat in a chemical process is a measure of the affinity, one can easily understand that the leading thermochemists, Berthelot and Thomsen, have made use of this and similar measurements<sup>1</sup> in support of their view, which was put forward earlier by Helmholtz and Lord Kelvin (Wm. Thomson).

There are, however, a large number of cases in which the agreement mentioned does not exist, as we have seen above in the case of the decomposition of water. Helmholtz<sup>2</sup> has deduced the following formula by means of the second law of thermodynamics :—

$$\frac{23,070de}{dT} = \frac{23,070e - W}{T}$$

where  $e$  represents the electromotive force of the combination,  $T$  the absolute temperature, and  $W$  the heat evolved in the chemical transformation of one gram-equivalent. This formula has been verified in a large number of cases.

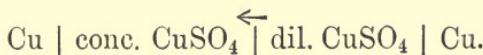
If  $\frac{de}{dT}$  i.e. the increase in the electromotive force (or in the affinity) for one degree Centigrade, is zero, the proposition of the thermochemists (the so-called Thomson's rule) is valid. As a

<sup>1</sup> Jul. Thomsen, *Ann. Physik. u. Chem.* (3), 1880, **11**, 246.

<sup>2</sup> Helmholtz, *Sitz.-Ber. d. Berl. Ak.*, 1882.

matter of fact, this is very nearly the case in the Daniell cell, and in some similar combinations investigated by Thomsen.

An investigation by Helmholtz<sup>1</sup> on the electromotive force of the so-called concentration cells has played a very important part. In these cells two solutions of the same salt, but of different concentrations, are in contact with each other and with the metal contained in the salt. Such a cell is, for example, the combination—



When the circuit of this cell is closed, the current flows in the direction of the arrow. Copper goes into solution on the right side, and is deposited on the left, the concentrated solution thus becoming diluted, and the dilute solution concentrated. The same result may be obtained by allowing water to evaporate (with the vapour pressure  $P$ ) from the dilute solution, and be condensed in the concentrated solution (vapour pressure  $p$ ). The work done per gram-molecule of water (18 gms.) distilled over is—

$$A = 1.99T \log_e \frac{P}{p}$$

There are two methods of calculating the work done in the transference of the water: firstly, by measuring the electromotive force of the concentration cell; secondly, by measuring the vapour pressure of the solutions in question. Obviously, it is possible to find the relation between these magnitudes in this way, which relation Helmholtz has indeed deduced. Nernst,<sup>2</sup> Planck,<sup>3</sup> and others have since done important work on this particular subject.

There are a large number of so-called molecular compounds in which chemical substances are combined with so-called water of crystallization, alcohol or ether of crystallization, or with ammonia or organic bases, etc. In these cases the substance added on, e.g. water, alcohol, etc., can be driven out of the compound by evaporation. The vapour pressure ( $p$ ) during this

<sup>1</sup> Helmholtz, *Ann. Physik. u. Chem.* (3), 1878, **3**, 201.

<sup>2</sup> Nernst, *Zeit. physikal. Chem.*, 1888, **2**, 613; 1889, **4**, 129.

<sup>3</sup> Planck, *Ann. Physik. u. Chem.* (3), 1890, **40**, 561.

process can be measured, and from a knowledge of the vapour pressure ( $P$ ) of pure water, alcohol, etc., it is possible, by means of the above formula, to measure the work done, *i.e.* the affinity exerted, in the formation of the compound. This work is often called the "free energy," a term due to Helmholtz.

Considering further the question of water of crystallization, it is well known that many substances can add on different quantities of water. The stability of the resulting compounds, which can be measured by the pressure of the water vapour, varies. For instance, the various compounds of copper sulphate containing water of crystallization have, according to Pareau,<sup>1</sup> the following pressures of aqueous vapour at 50° C. :—

$\text{CuSO}_4 + 1\text{H}_2\text{O}$	$\text{CuSO}_4 + 3\text{H}_2\text{O}$	$\text{CuSO}_4 + 5\text{H}_2\text{O}$
4·4 mm.	30 mm.	47 mm.
(pure water)		
91 mm.		

The heat evolved by the addition of the different molecules of water also varies, as Thomsen's measurements show. Thus in the case of sodium phosphate,  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O}$ , the heat evolved by the addition of the first two  $\text{H}_2\text{O}$  molecules to the anhydrous salt is 3010 cal. per molecule, and by the remaining ten molecules 2240 cal. per molecule. In the case of sodium carbonate,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ , the addition of the first molecule of water causes a heat evolution of 3390 cal., whereas for each of the following seven molecules the evolution is only 2120 cal., and for each of the last two molecules 1700 cal. From Pareau's<sup>1</sup> results, the work which may be obtained by changing one gram-molecule (18 grms.) of water (vapour pressure  $P$ ) into water of crystallization at the absolute temperature  $T$  (vapour pressure  $p$ ) can be calculated. This work, which is equal to the difference between the free energy of the water and that of the water of crystallization, is much less than the heat evolved ( $W$ ) at the same time, as the figures given below (Thomsen<sup>2</sup>) show. As can readily be seen, this heat is equal to the difference between the heats of solution of  $\text{CuSO}_4 + n\text{H}_2\text{O}$  and  $\text{CuSO}_4 + (n + 1)\text{H}_2\text{O}$ .

<sup>1</sup> Pareau, *Ann. Physik. u. Chem.* (3), 1877, 1, 39.

<sup>2</sup> Thomsen, *J. pr. Chem.* (2), 1878, 18, 1.

Salt.	Heat of solution.	Heat evolved on the addition of 1 mol. H <sub>2</sub> O.	Work done on the addition of 1 mol. H <sub>2</sub> O.
CuSO <sub>4</sub> . . .	15,800 cal.		
CuSO <sub>4</sub> + H <sub>2</sub> O . .	9,330 „	6470 cal.	1940 cal.
CuSO <sub>4</sub> + 2H <sub>2</sub> O . .	6,160 „	3170 „	710 „
CuSO <sub>4</sub> + 3H <sub>2</sub> O . .	2,810 „	3350 „	710 „
CuSO <sub>4</sub> + 4H <sub>2</sub> O . .	630 „	2180 „	423 „
CuSO <sub>4</sub> + 5H <sub>2</sub> O . .	- 2,750 „	3380 „	423 „

This case is a good example for showing that the work done in a chemical process cannot be put equal to the heat evolved. This latter view was maintained for a long time by thermo-chemists. The predictions which they made by the use of this rule on the stability (strength) of different compounds, and thence on the course of chemical reactions, are only true at the absolute zero, as van't Hoff has shown.<sup>1</sup> The ordinary temperature of the earth may be considered as relatively close to that of the absolute zero, and therefore these predictions are correct in many cases.

An example from physics, which illustrates the importance of the free energy, is the change of water into ice. At 0° C. the vapour pressures of ice and water are equal (4·6 mm.), *i.e.* there is equilibrium, and A becomes zero. W, however, is equal to the latent heat of liquefaction,  $18 \times 79\cdot7 = 1435$  cal. At -10° C., P = 2·197 and p = 1·997; therefore A = 49·7 cal., while W =  $18 \times 75 = 1350$  cal.

In a similar way one can recalculate the results of Isambert<sup>2</sup> for the vapour pressures of the compounds 2AgCl + 6NH<sub>3</sub> (801 mm. at 21° C.) and 2AgCl + 3NH<sub>3</sub> (95 mm. at 21° C.), since the pressure of saturated ammonia vapour at this temperature is found, from the results of Regnault, to be 6589 mm. The work which may then be obtained by the addition of a molecule of NH<sub>3</sub> is calculated to be 2470 cal. for each of

<sup>1</sup> If T = 0 is substituted in the equation on p. 66, then W = 23,070e, *i.e.* the evolution of heat is a measure of (proportional to) the affinity at T = 0.

<sup>2</sup> Compare Wurtz, "Dictionnaire de Chimie," tome 1, p. 1178.

the first three molecules of  $\text{NH}_3$ , and 1227 cal. for each of the three last. These values are of the same order as those calculated above.

In recent times Horstmann<sup>1</sup> and Jarry<sup>2</sup> have carried out investigations on these compounds. According to the latter, the vapour pressures of the two ammonia compounds at 0° C. are 262 and 12 mm. respectively (the vapour pressure of pure ammonia at the same temperature is 3185 mm.), and at 21° C. 927 and 53·4 mm. respectively (and 6516 mm.). From this the work is calculated to be 1357 and 3032 cal. respectively at 0° C., and 1147 and 2818 cal. respectively at 21° C. It is very characteristic that the work (affinity) decreases with increasing temperature. At a high enough temperature (the so-called transition point) the affinities in question would become zero, *i.e.* the compound would no longer be able to exist; the compound richer in ammonia would first become unstable, and then the one poorer in ammonia.

As we shall see later, solubility corresponds to vapour pressure in many points, and can also be used for measurements of affinity.<sup>3</sup>

The chemical properties of hydrated salts can be approximately represented as the sum of the properties of the two components, *e.g.* of the anhydrous salt and of the added water. As is well known, however, it is characteristic of chemical compounds that the properties of the components have almost completely disappeared. One, therefore, readily assumes that in salts containing water of crystallization the components of the water-molecules have not been transposed, but remain unchanged, and in the same position as they did in the water before it combined with the salt. The same holds true for the salt. The difficulty then occurs, however, of finding places at which the many molecules of water can be added on according to the rules of valency, *e.g.* the twelve  $\text{H}_2\text{O}$  to  $\text{Na}_2\text{HPO}_4$ . The idea that such compounds were held together by valencies was therefore given up altogether, and they were called molecular compounds. To these molecular compounds were also added those which could

<sup>1</sup> Horstmann, *Ber.*, 1876, **9**, 749.

<sup>2</sup> Jarry, *Ann. Chim. Phys.* (7), 1899, **17**, 327.

<sup>3</sup> Compare Frowein, *Zeit. physikal. Chem.*, 1887, **1**, 5.

not be represented by a simple formula, using the ordinary valencies. Such were many double salts, especially those with monovalent negative ions, as double nitrates, double chlorides, etc.

The investigations of Hittorf on the migration of ions nevertheless showed that in many cases the so-called molecular compounds behaved on electrolysis as if they were composed of two ions, the one consisting of hydrogen, or of the most positive metal of the compound, and the other of the remainder of the compound. He investigated, for example, the following compounds which were at that time considered to be molecular compounds:  $\text{KC}\ddot{\text{N}} + \text{AgCN}$ ,  $\text{PtCl}_4 + 2\text{NaCl}$ ,  $\text{AuCl}_3 + \text{KCl}$ , and showed that their ions are:  $\overset{+}{\text{K}}$  and  $\text{Ag}(\text{C}\ddot{\text{N}})_2$ ,  $2\overset{+}{\text{Na}}$  and  $\overset{-}{\text{PtCl}}_6$ ,  $\overset{+}{\text{K}}$  and  $\text{Au}\bar{\text{Cl}}_4$ . Obviously, in these three ions the negative ions of the alkali salt used have combined with the molecules of the compound of the noble metal, and consequently one can assume that this is also the case in the undissociated double salts. It was altogether contrary to the ideas which prevailed at that time (1854) that such a mild chemical process as solution in water at low temperature should tear asunder the atoms of the alkali salt entering into the composition of the double compound. The doctrine of valency did not at that time offer any explanation of the composition of complex ions.

## CHAPTER VII

### *THE DEVELOPMENT OF THE DOCTRINE OF VALENCY*

As old as is the observation that two different substances combine with each other, *i.e.* become a new and definite substance, losing at the same time their most striking physical properties, just so old is the symbolic representation of the union by joining together two symbols. In olden times the symbols of the metals were identical with the signs used for the planets. It was gradually recognized that not only one, but often two or more new compounds could result from the union of two substances. In some such cases Proust proved that the different products of combination differed from each other in the relative quantities of their components, and that each one was characterized by a definite ratio of the weights of the components. He recognized such an invariable composition as the sign of a definite chemical compound (Proust's law of constant proportions). Dalton extended Proust's law by the discovery of multiple proportions. In order to represent it he made use of symbols, which correspond to the formulæ of the present day; his symbols for the elements corresponded to the old alchemical ones, however, whilst we are indebted to Berzelius for the present convenient ones, which make use of the letters of the alphabet. In Gay Lussac's discovery of the law of simple volumes in which gases combine with each other, Berzelius saw a further reason for the formulation of chemical compounds according to Dalton's method (cf. chap. II.).

This, as we can say to-day, wholly correct method of representing chemical compounds was again given up immediately after, because pure empiricism was unduly emphasized, to the

neglect of theoretical methods of consideration. Instead of the atomic weights, the so-called equivalent weights were used, and one came back to the standpoint of Proust and Richter, without paying any attention to the later developments of the theory of chemical compounds. In order to represent the compounds of two elements, their symbols were simply written side by side, and if several were known, containing the elements in different proportions, different symbols for the same element were used. Thus the two compounds of iron and chlorine, ferrous and ferric chlorides, were written  $\text{feCl}$  and  $\text{FeCl}$ . It is rather remarkable that even at the present day, especially in French works, remains of this method of representation are found.

With the rapid development of organic chemistry it soon became impossible to be satisfied with this method of representation. The hypothesis of Avogadro, which had been either neglected for a long time or else forgotten, was found to be very useful for obtaining a summary of known facts. The use of this hypothesis led to consequences such as, for example, that an atom of oxygen is linked to two atoms of hydrogen in a molecule of water. An atom of oxygen is thus able to bind two atoms of hydrogen, or, according to the usual method of expression, in water an atom of oxygen is equivalent to two atoms of hydrogen. In order to represent this, it was assumed that each atom of oxygen possesses two places of linkage or valencies, while hydrogen has only one. Now, hydrogen and oxygen occur together with carbon in very many organic compounds; many of them are volatile, and their molecular weight can be determined by means of Avogadro's hypothesis. Kekulé succeeded in representing all these compounds by means of formulæ in which carbon was given four, oxygen two, and hydrogen only one valency; *i.e.* carbon is said to be tetravalent, and so on. He was further successful in representing the compounds of other elements with carbon, oxygen, and hydrogen by formulæ, in which each element possessed a definite valency, and which were never in disagreement with the vapour-density determinations. This doctrine of constant valency, especially of the tetravalency of carbon, proved extraordinarily fruitful in the development of organic chemistry, and was therefore applied to inorganic

chemistry. We now know that it is no longer tenable, but it is instructive to see how long it was retained by the help of special hypotheses, which were put forward as a matter of experience, without, unfortunately, any attempt being made to prove them. The endeavour to fit the formulæ of chemical compounds into the scheme of Kekulé's valency numbers resulted in a "formulæ painting" (to use Kolbe's expression) which is now often amusing to us, but at that time was praised as an important theoretical development.

One of the first difficulties was the behaviour of carbon monoxide, which, according to the accepted atomic weights and Avogadro's hypothesis, possessed the formula CO. If C possesses four, and O only two valencies, two valencies of C must remain "unsaturated." This could be represented by imagining that the two valencies combined with each other. If one assumes that the valencies depend on electric charges, and if, with Berzelius, oxygen is considered to be negatively charged, then oxygen has two negative elementary charges, which are bound by two positive elementary charges situated on the carbon atom. There are two more elementary charges on the carbon atom, the one positive and the other negative, which neutralize each other. We have mentioned above the view of Helmholtz, that compounds with an even number of unsaturated valencies, just as many positive as negative, possess elementary charges which mutually bind each other.

Since the same carbon atom carries both a positive and a negative elementary charge, they must be localized at different places on the atom and insulated from each other. According to this view, therefore, the valencies must be fixed to definite points on the atom, and the other atoms or atomic complexes, which are held fast by means of the valency charges, must be oriented in a definite manner round the central atom to which they are fixed. The doctrine of the orientation of atoms in space, *i.e.* of stereochemistry, has proved fruitful in many directions. It owed its origin to the attempts of van't Hoff<sup>1</sup> and Le Bel<sup>2</sup> to explain optical isomerism. This deals with compounds which

<sup>1</sup> Van't Hoff, "Voorstel tot uitbreiding der structuur-formules in de Ruimte," Sept., 1874. Cf. Van't Hoff, "Chemistry in Space."

<sup>2</sup> Le Bel, *Bull. Soc. Chim. Paris*, Nov., 1874.

have the same composition and are alike in every other property, with the exception of the effect they have on the rotation of the plane of polarization of light.<sup>1</sup> They possess numerically equal rotations, but of opposite sign. It is assumed that the two bodies can only differ from each other in the sense that the molecule of the one is so built up that it forms the mirror image of the other; the two molecules stand in the same relation to each other as do the right and left hands. In explanation of this, it is supposed that the four valencies of carbon are oriented with respect to each other like the corners of a regular tetrahedron, this being at the same time the simplest arrangement of four points in space. Four different atoms, A, B, C, and D, situated at the corners of such a regular tetrahedron, can group themselves in two different configurations, as shown in the opposite figure (Fig. 9). (The edges represented by the dotted lines are supposed to lie towards the back.) The order of B, C, and D, as seen from A, is left to right C, i.e. in the same sense as the movement of the hands of a watch, in the one case, and from right to left C in the other. It is easy to see that the two tetrahedra become congruent when A and B are the same; one only needs to turn the figure on the right so that what was originally B comes to the top. Hence it follows that isomerism can only occur when the four valencies of the carbon atom are joined to four different atoms or atomic complexes.

Van't Hoff has tested this conclusion in a large number of cases, and always found it verified.

If two valencies of the one carbon atom are connected with two valencies of another carbon atom, as is the case in the so-called ethylene compounds, a configuration similar to that shown in Fig. 10 results. The two valency positions A and A<sub>1</sub> are very close to each other, as also are the two valency positions B and B<sub>1</sub>. The other four, and the atoms C, D, E, and F which are

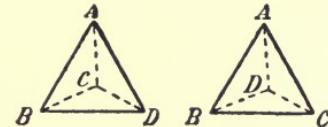


FIG. 9.—Model of the asymmetric carbon atom.

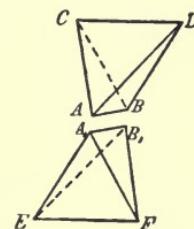


FIG. 10.—Model of the ethylene linking.

<sup>1</sup> The absorption of circularly polarized light may also be different for the two isomers (Cotton, *Ann. chim. Phys.* (7), 1896, **8**, 373).

connected to them, may be considered to lie in one plane. For the sake of simplicity, we assume that C is equal to E, and D to F. Obviously two isomers can result, C being either in the neighbouring position to E, as in the figure, or to F, E and F having changed places. The best-known example of this kind is the isomerism of fumaric and maleic acids, in which C and E are hydrogen atoms, while D and F are carboxyl groups (COOH). Maleic acid conducts electricity better than fumaric, and hence it is concluded, by analogy with similar cases, that in maleic acid the carboxyl groups are in the neighbouring position to each other (the so-called *cis*-form), whilst in fumaric acid they lie as far apart as possible (*trans*-form). The same conclusion had previously been arrived at on purely chemical grounds. J. Wislicenus and his students have done a large amount of research on this subject.

Each valency linking can be broken ; this is true in all cases, since it is a necessary condition for every chemical reaction. An atom or an atomic complex is thereby removed from the molecule, and its place taken by another atom or atomic complex. One must consequently assume, as was first pointed out by Williamson, that the atoms or complexes separate themselves from the molecule from time to time, even when they do not react with other molecules. Consider now a molecule in which the four different atoms, A, B, C and D, are bound to one carbon atom. The atoms A and B, which may possess equal electric charges, *e.g.* positive, are therefore separated at times from the molecule, and it may happen that they are both separated at one and the same time. It is therefore possible for them to change places on combining with the carbon atom again. This is synonymous with a transformation of the original molecule into its optical isomer. Since now two optical isomers are equal to each other in all respects, excepting their asymmetry, and possess absolutely the same stability, this reaction must go on until an equal number of the two kinds of molecules are present in the same solution. Optically active bodies of this kind must therefore change into mixtures of equal quantities of dextro- and laevo-molecules, *i.e.* into optically inactive mixtures (called racemic mixtures). That optical isomers are known depends solely on the fact that the

velocity of reaction at lower temperatures is in most cases too small to be noticeable. On the other hand, at higher temperatures the reaction generally proceeds smoothly; thus, for example, the optically active mandelic acids become inactive at  $180^{\circ}$ . It is generally possible to prepare the inactive from the active modifications by heating the latter either with or without the addition of chemical reagents.

The matter is altogether different in the *cis*- and *trans*-modifications. The atoms, or atomic complexes, occupy different positions with respect to each other, and not the same, as is the case with the optical isomers. The two isomeric bodies have, therefore, essentially different physical and chemical properties, especially different stabilities. At ordinary temperatures, fumaric acid is more stable than maleic in aqueous solution, and the latter acid can be changed into the former by the addition of strong acids, which act catalytically, as Kekulé has shown. Heating a 10 to 30 % solution to  $200^{\circ}$  acts in the same way. On the other hand, it is possible to change fumaric acid into maleic anhydride by distillation, whereby the tendency of maleic acid to split off water at higher temperatures becomes active. Maleic acid can again be obtained from the anhydride.

I cannot agree that these transformations in any way contradict the idea of localized valencies in the atom, as Werner maintains.

In later times stereochemical conceptions have been successfully extended to atoms other than carbon, especially to the nitrogen atom.<sup>1</sup>

It is noteworthy that optically active bodies are never obtained by chemical processes in which only optically inactive bodies are used. The probability of a dextro-rotatory molecule being formed is just as great as that of a laevo-rotatory. It is otherwise if the newly formed substance can combine with an optically active substance. The relative position of the atoms of the laevo-rotatory molecule to the atoms or atomic groups of the asymmetric molecule present is obviously different from that of the dextro-rotatory molecule; the one compound will

<sup>1</sup> Wedekind, *Ber.*, 1904, **39**, 474. In this connection see also Pope and others on optically active nitrogen, sulphur, tin, and selenium compounds (*Journ. Chem. Soc.*, 1900, **77**, 1072, etc.).

therefore be formed in preference to the other. This explains the celebrated synthesis of optically active molecules by Emil Fischer.<sup>1</sup> The formation of optically active molecules by the chemical processes which take place in plants must be looked upon in a similar manner, as also the selective decomposition of an inactive mixture by living organisms (moulds), in which case an optically active residue is left.

We will now return to the "unsaturated" compounds, analogous to carbon monoxide, CO. It has been known for a long time that sulphur combines with hydrogen to form hydrogen sulphide, H<sub>2</sub>S, and with oxygen, giving the oxides SO<sub>2</sub> and SO<sub>3</sub>. Thus in these three compounds sulphur exercises two, four, or six valencies. Sulphur consequently possesses three different valency values, which differ from each other by two or four. This can obviously be looked upon in the same manner as the di- and tetra-valency of carbon, *i.e.* one assumes that the sulphur atom is in reality hexa- or octavalent, and in those cases where it shows a less valency the valencies left unsatisfied neutralize each other in pairs. Relations similar to those occurring in the case of sulphur are met with in a great number of elements, as may be seen in any text-book of inorganic chemistry.

Kekulé's doctrine of the constant valency of the elementary atoms was therefore given up, and it was assumed that the valency of an atom could change by even numbers. Thus chlorine, bromine, and iodine were considered to be 1-, 3-, 5-, and 7-valent, iron to be 2-, 4-, and 6-valent, gold to be 1- and 3-valent, tin and platinum 2- and 4-valent, etc. In order to include such iron compounds as FeCl<sub>3</sub> in this scheme, it was assumed that hexavalent double atoms  $\equiv$ Fe—Fe $\equiv$  were contained in it, and the formula of ferric chloride was written Cl<sub>3</sub>Fe—FeCl<sub>3</sub>.

The molecules of the simple bodies were considered to be made up of two atoms, by analogy with H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>, which had been the most studied. In the case of phosphorus, arsenic, and sulphur, the number of atoms in the molecule is still greater. Later it was found that cadmium and mercury, in the

<sup>1</sup> Fischer, *Ber.*, 1894, **27**, 3189. Cf. also McKenzie, *Jour. Chem. Soc.*, 1904, **86**, 1249.

form of vapour, consist of monatomic molecules. This was considered to be just as it should be, since it was assumed that the two valencies of these divalent atoms neutralized each other. This explanation was no longer valid, however, when Victor Meyer<sup>1</sup> showed that iodine and bromine consist of single atoms at high temperatures. The same is true for the vapour of the monovalent alkali metals. Later on measurements of the freezing-points of mercury solutions<sup>2</sup> led to the results that even below  $-40^{\circ}$  C., *i.e.* at very low temperatures, nearly all the metals consisted of monatomic molecules. V. Meyer,<sup>3</sup> using his method for determining vapour densities, found that molecules having the formulæ  $\text{FeCl}_2$ ,  $\text{Fe}_2\text{Cl}_4$  and  $\text{FeCl}_3$  existed in gaseous condition. Nilson and Pettersson,<sup>4</sup> using the same method, found that the chlorides of indium correspond to the formulæ  $\text{InCl}$ ,  $\text{InCl}_2$ , and  $\text{InCl}_3$ , those of gallium to the formulæ  $\text{GaCl}_2$  and  $\text{GaCl}_3$ , and those of chromium to the formulæ  $\text{CrCl}_2$ ,  $\text{Cr}_2\text{Cl}_4$ , and  $\text{CrCl}_3$ . The whole doctrine of valency thereby lost its stability. One assumed that in some relatively few cases the valency could be of any desired value. Occasionally it was assumed that the valency had a definite and fixed maximum, *e.g.* 8 according to Abegg.<sup>5</sup> In recent times some experimenters have shaken the solid rock of the doctrine of valency, viz. the tetravalency of the carbon atom, in that they assume trivalent carbon; however, they do not seem to have sufficient grounds for their assumption.

It would probably be still more difficult to bring into line the compounds with so-called water of crystallization, alcohol of crystallization, ammonia, etc.

Recently different attempts have been made to overcome these difficulties; in this connection mention should especially be made of Werner<sup>6</sup> and, from the electrochemical side, of

<sup>1</sup> V. Meyer, *Ber.*, 1880, **13**, 394.

<sup>2</sup> Tammann, *Zeit. physikal. Chem.*, 1882, **3**, 441.

<sup>3</sup> V. Meyer, *Ber.*, 1884, **17**, 1335.

<sup>4</sup> Nilson and Pettersson, *Compt. rend.*, 1888, **107**, 500 and 527.

<sup>5</sup> Abegg., *Zeit. anorg. Chem.*, 1904, **39**, 367.

<sup>6</sup> Cf. Werner, *Vierteljahrsschr. d. Zürcher naturf. Ges.*, **36**, 1891.

“Neuere Anschauungen auf dem Gebiete der anorg. Chem.” (*Die Wissenschaft*, vol. viii.). Braunschweig, 1905.

Abegg.<sup>1</sup> All return to an idea of Berzelius, which in a certain sense formed the basis of his dualistic system. Berzelius' scheme, expressed in modern symbols, is as follows: Under the influence of electric charges, potassium and oxygen combine to form  $K_2O$ , and similarly sulphur and oxygen combine, forming  $SO_3$ . When  $K_2O$  and  $SO_3$  are brought together the two molecules unite, because of a residual positive charge on the  $K_2O$  and a residual negative charge on the  $SO_3$ . In support of this view, Berzelius mentioned that in the electrolysis of potassium sulphate, caustic potash ( $K_2O$ , according to Berzelius) appeared at the negative pole, and sulphuric acid ( $SO_3$ , according to Berzelius) at the positive pole. This compound,  $K_2O \cdot SO_3$ , can further combine with a similar compound,  $Al_2O_3 \cdot 3SO_3$ , whereby ordinary potassium alum results. Berzelius therefore assumed that the original valencies (electric charges) of the elementary atoms had mutually combined with each other in the so-called binary compounds (oxides), but that still weaker residual valencies (residual charges) remained over, which united the binary compounds to ternary, e.g. to salts. Two salts can again be linked together by means of residual affinities, forming double salts. This conception was founded on the wide chemical experience which Berzelius possessed. It is very interesting to notice that the empirical material which has hitherto accumulated forces one, at the present time, to a conception which is in the main points identical with that of Berzelius. The conceptions of Berzelius of original and residual charges correspond to the present-day conceptions of principal and subsidiary valencies (Werner), or of normal and contra-valencies (Abegg).

Berzelius' idea that  $K_2O$  and  $SO_3$  are respectively positively and negatively charged was disproved by Daniell, who showed that copper sulphate is split up into copper and  $SO_4$ , the latter being evolved at the positive pole, where it acts secondarily on the water, with the formation of sulphuric acid and oxygen. In exactly the same way potassium sulphate is split up into potassium and  $SO_4$ , which react secondarily with the water, forming caustic potash and hydrogen

<sup>1</sup> Abegg, *Christiana Vidensk. Selsk. Skrifter math.-naturv. Kl.*, No. 12, 1902; Abegg and Bodländer, *Zeit. anorg. Chem.*, 1899, **20**, 496.

at the negative pole, and sulphuric acid and oxygen at the positive. To-day there can be no doubt but that Daniell's conception is the correct one. On this account Werner assumes that the subsidiary valencies do not possess electric charges. "Principal valencies," says he, "join together the simple or composite radicles which are able to occur as independent ions, or whose power of chemical combination is equivalent to that of the ionizable radicles." Other valencies are subsidiary valencies. On the other hand, Abegg assumes that the "contra-valencies" are characterized by the possession of charges opposite in sign to those of the normal valencies. Each atom is supposed to possess eight valencies altogether. One cannot understand how these assumptions do away with the difficulties of Berzelius' theory. On the other hand, it must be conceded that Abegg is right in assuming that such an essential difference between principal and subsidiary valencies could scarcely exist, as would be the case if the one were caused by electrical forces, and the other were quite independent of such forces. Firstly, in many cases it is difficult to say whether principal or subsidiary valencies are being exerted, no general characteristic being known which allows of a definite decision; only in the case of the metallic elements, the halogens, and of analogous atomic complexes such as ammonium and cyanogen, does the ionized condition form a sure criterion. Secondly, the compounds formed by means of the subsidiary valencies conform to Dalton's law of multiple proportions, and this points to forces which must act analogously to electrical ones.

In order, if possible, to find a way out of these difficulties, we will consider the linking between hydrogen chloride and ammonia, which, according to the old ideas, is brought about by principal valencies, but, according to Werner, depends on subsidiary valencies. The evolution of heat on combination is no less than 41,800 cal.,  $\text{NH}_3$  and  $\text{HCl}$  being in the gaseous condition, and  $\text{NH}_4\text{Cl}$  in the solid state. On being vaporized, this compound partially decomposes into its two components, and this has given support to the idea that it is a molecular compound. In aqueous solution  $\text{NH}_4\text{Cl}$  dissociates electrolytically into  $\text{NH}_4^+$  with a positive charge, and  $\text{Cl}^-$  with a negative charge. Two views have been put forward with respect to

the constitution of the  $\text{NH}_4$  ion; firstly, the one which has been prevalent up to now, whereby N combines with four positive H-atoms by means of four negative valencies, but still possesses another positive charge with which it can link the negatively charged chlorine ion; secondly, the ones put forward by Werner and Abegg, whereby the neutral  $\text{NH}_3$  binds H by means of a subsidiary or contra-valency, the hydrogen being positively charged, and therefore able to add on the negative chlorine ion. According to Werner, no electric charges are brought into action by the subsidiary valencies, while, according to Abegg, the H linked by the contra-valency possesses a negative charge, and the corresponding place of linkage on the N a positive charge. In both cases the fourth hydrogen is differently linked from the three hydrogens in ammonia, and one would therefore expect that the substitution of hydrogen in  $\text{NH}_4\text{Cl}$  by a monovalent radicle  $\text{R}-\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_6\text{H}_5$ , etc.—would result in two isomeric substitution products, corresponding to the formulæ  $\text{NH}_2\text{R.HCl}$  and  $\text{NH}_3\text{RCl}$ . Since such isomerism is not known, we must conclude that the four H-atoms in the ion  $\text{NH}_4$  are similarly linked to the N-atom. Werner endeavours to support his formula by the following argument: HCl is strongly dissociated,  $\text{H}_2\text{O}$  hardly at all, and these properties are retained when ammonia is added, forming ammonium chloride,  $\text{NH}_3\text{HCl}$ , and ammonium hydroxide,  $\text{NH}_3\text{H}_2\text{O}$ , respectively. He, however, does not take into account the fact that the dissociation constant of ammonia ( $23 \times 10^{-6}$ ) is more than  $10^{11}$  times that of water at  $25^\circ$ . The inadequacy of Werner's theory is also shown by the fact that if hydrochloric acid is replaced by a weak acid, *e.g.* acetic acid, the degree of dissociation of the weak acid is very much increased by neutralization with  $\text{NH}_3$ . Indeed, a substance like tetramethylammonium hydroxide,  $(\text{CH}_3)_4\text{NOH}$ , is one of the strongest bases, and its degree of dissociation is similar to that of the salts, although, according to Werner, it must be considered as an addition product of trimethylamine ( $K = 74 \times 10^{-6}$ ) and methyl alcohol, which is probably less dissociated than water. (In passing, it may be noticed that a similar conclusion of Werner's is not well founded, according to which tetrahydroxylamine platinum hydrate possesses a different constitution from the corresponding

chloride ( $\text{HOH}_2\text{N}$ )<sub>4</sub>PtCl<sub>2</sub>, because the one is only very slightly dissociated, much less so than an alkali hydroxide, while the other is strongly dissociated. One could conclude in an analogous manner that every weak acid, *e.g.* acetic acid, has an essentially different constitution from its salts, *i.e.* that the relative position of the atoms is different.)

We cannot, therefore, assume otherwise than that in the ammonium ion, as it exists in aqueous solution, four positive hydrogen ions, occupying similar positions, are linked by four negative valencies of the nitrogen, which also possesses a positive ionic charge. Now, there are numerous indications that the valencies exist before any compound is formed. I have found, for example, that in the Bunsen flame undissociated molecules of sodium hydrate emit just as strong a light as those which have dissociated into sodium and hydroxyl. One assumes that the luminosity is due to the vibrations of the charges, and consequently that the sodium in the glowing sodium hydroxide is electrically charged. If, therefore, we take away a positively charged hydrogen atom from the ammonium ion, electrically neutral ammonia with a negative and a positive elementary charge, which are placed at different positions on the nitrogen atom, probably results.

Suppose we bring a hydrogen chloride molecule from an infinite distance into the neighbourhood of the ammonia molecule. According to the prevailing ideas, the former molecule possesses a positive charge on the H atom and a negative one on the Cl atom, and these charges, together with the atoms on which they are, will so arrange themselves that the Cl will come close to the positive valency, and the H to the negative. The strength of this linking may be of the same order as that between a positive and a negative valency, corresponding to the "principal valency"-linking. We will assume that the two charges in the NH<sub>3</sub> and HCl are at an equal distance from each other, and that the molecules approach each other so that the median plane  $\epsilon$  between the two charges on H and Cl, and the plane of symmetry  $\epsilon'$ , which lies between the two charges on the NH<sub>3</sub>, coincide with each other. We then obtain the following values for the potential energy P, taking as our unit the potential energy of two elementary charges the

same distance apart. We denote the distance apart of the two charges on H and Cl, as also of the charges on  $\text{NH}_3$ , by  $d$ , the distance of the double charges from each other being  $e$ .

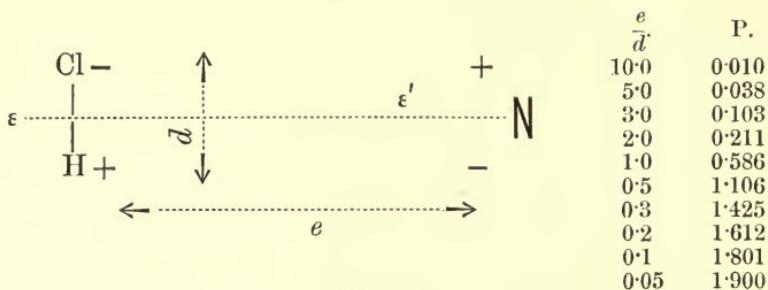


FIG. 11.

As may be seen from the table, the double linking, for so it may be conveniently designated, is much weaker than the single linking as long as the distance apart  $e$  of the two molecules (or really of their charges) is greater than the distance apart  $d$  of the two charges in the molecule. As the value of  $e$  approaches zero, the energy necessary for dissolving the double linking approximates more closely to twice the value necessary for dissolving the single linking. When  $\frac{e}{d} = 0\cdot514$ , the two energies become equal.

Now, it is natural to assume that the molecules cannot come nearer to each other than the distance between two valencies in the same atom. One can therefore comprehend why the double linking is generally much weaker than the single one. It is obvious that the double linking cannot be broken by means of external electrical forces, because in dissolving it just as much positive as negative electricity is transferred at one and the same time. The fall in potential can therefore cause no work to be done, from which it follows that the electrical driving force is zero.

It is a peculiarity of electrical double linkings that the linkings within the individual molecules remain completely undisturbed when the one molecule, *e.g.* HCl, links itself to the other, *e.g.*  $\text{NH}_3$ . (Secondary changes can occur, as, for example, the splitting off of ions.) One can therefore say that in these linkings, which correspond to molecular ones, the linked bodies remain unchanged, as, for example, salt and water in salts

containing water of crystallization. If one charge is split off, as in  $\text{NH}_4\text{Cl}$ , the double linking will naturally be dissolved, and the one partial molecule (here H) comes into closer connection with the second unchanged molecule (here  $\text{NH}_3$ ). If, on the other hand, no supplementary reaction take place, all the principal properties of the molecules joined by a double linking are retained, and one can consider them to still exist in the compound. The double linking is thus distinguished from the single, *e.g.* from the linking of a K atom with an I atom.

There are relatively few molecules which possess the property of coupling up with other similar molecules or atoms by means of double linkings. Water is the chief one, and therefore one must consider that oxygen possesses a double valency, with a positive and a negative charge, besides the two negative valencies. Recently many investigators have felt themselves compelled to assume oxygen to be tetravalent, *e.g.* Baeyer and Villiger.<sup>1</sup> The substitution products of water behave similarly to water itself; the alcohols, ethers, esters, oxygen acids and their salts, sugars, etc., can be considered as such. The addition of a large number of water molecules, as, for example, in the salts with water of crystallization, may be represented in such a manner, that a whole chain of oxygen atoms (in water) link up with each other by means of the two alternately positive and negative valencies which are in excess, and at the end of the chain a double valency remains over and binds the salt.<sup>2</sup> Such linkings must be assumed to be present in aqueous vapour of high density, and probably also in liquid water, in order to enable one to understand the existence of double and treble molecules,  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ . Similar double linkings couple together the molecules of the alcohols and of organic acids, either when in the state of vapour or when dissolved in solvents other than water, to double molecules or still higher complexes. It must also be assumed that in some compounds sulphur and selenium possess double valencies similar to those of oxygen.

<sup>1</sup> Baeyer and Villiger, *Ber.*, 1901, **34**, 2679, 3612; 1902, **35**, 1201.

<sup>2</sup> In order to avoid this assumption, one may possibly suppose that the charges of the principal valencies of a salt molecule attract the corresponding charges of the water.

Similarly, in ammonia and all its substitution products, including carbamide, everything points to nitrogen possessing typical double valencies of the most active kind. Salts possessing "ammonia of crystallization" split off ammonia as vapour almost according to the same rules that regulate the giving off of water from salts containing water of crystallization. In many cases the compounds of phosphorus, arsenic, antimony, and bismuth, which correspond to ammonia, behave similarly. Further, it is well known that the fluorides, chlorides, bromides, iodides, cyanides and sulphocyanides form a large number of molecular compounds. In order to explain the oxygen compounds of the halogens, heptavalency has already been ascribed to them. In general one notices that the double valencies of the halogens are inclined to link themselves to double valencies of the same atoms. The reason of this is probably, that when the charges in the two molecules are exactly at the same distance apart, a close union can more readily take place.

These double valencies obviously explain the observation that the valency so often alters by even numbers. All the difficulties connected with the doctrine of valency as hitherto put forward, are not removed, however, by the views proposed above. For example, it does not seem possible to carry through the natural assumption that a given valency always possesses the same charge, and is not sometimes positive and sometimes negative. As regards the molecules  $H_2$ ,  $N_2$ , and  $O_2$ , for example, one can scarcely make any other assumption than that the one atom is positively and the other negatively charged.

According to the electron theory, varying valency would be explained by assuming that a mono-, di-, or trivalent negative ion consists of a combination of the atom or atomic complex in question with one, two, or three electrons, which are all negative. A positive ion is formed from a given atom or complex by the splitting off of the necessary number of electrons (cf. Chap. VIII.). This conception has hitherto remained only a formal one, and has led to no new results.

The doctrine of valency was verified by the regularities which are brought to light by the system of Mendeléeff (cf. Chap. VIII.). The elements in the first vertical column possess

no valency, those in the second are monovalent, in the third divalent, and so on. Accordingly, there can be no doubt that carbon may possess four principal valencies, although the electrolytic test, which, according to Werner, decides the matter definitely, can never be made, since carbon compounds conduct electricity so badly. In the same way the number of (principal) valencies of the other elements, which are not known as ions, is determined.

If one were to ascribe a large number of valencies to the elements, it would obviously be possible to explain all possible atomic combinations. The use of the doctrine of valency, in that it enables one to take a general survey of the subject, would thereby be completely lost. It is therefore evident why an endeavour has been made to limit the number of valencies as much as possible. Thus hydrogen has always been considered monovalent, because this is sufficient in all cases. Werner does away with this fundamental proposition of the doctrine of valency, in that he assumes that in the ammonium ion a hydrogen atom is linked to  $\text{NH}_3$  by means of a subsidiary valency, and at the same time possesses a free principal valency by means of which it can unite with a negative ion. Also Abegg assumes—not less than seven!—contravalencies in the case of hydrogen. Similarly Werner limits the number of subsidiary valencies by assuming a maximum co-ordination number 6. This number is found, for instance, in the ion  $(\text{CN})_6\text{Fe}$  of the salt  $\text{K}_4(\text{CN})_6\text{Fe}$ , and in the ions  $(\text{H}_3\text{N})_6\text{Pt}$ ,  $(\text{H}_3\text{N})_5\text{Cl}\text{Pt}$ ,  $(\text{H}_3\text{N})_4\text{Cl}_2\text{Pt}$ ,  $(\text{H}_3\text{N})_3\text{Cl}_3\text{Pt}$ ,  $\text{H}_3\text{NCl}_5\text{Pt}$ , and  $\text{Cl}_6\text{Pt}$  of the salts  $(\text{NH}_3)_6\text{PtCl}_4$ ,  $(\text{NH}_3)_5\text{Cl}\text{PtCl}_3$ ,  $(\text{NH}_3)_4\text{Cl}_2\text{PtCl}_2$ ,  $(\text{NH}_3)_3\text{Cl}_3\text{PtCl}$ ,  $\text{KNH}_3\text{Cl}_5\text{Pt}$  and  $\text{K}_2\text{PtCl}_6$ . More than six atoms or atomic groups cannot be bound to the metal atom in the ions. Werner makes highly interesting applications of this theory to the ammoniacal compounds and analogous bodies. He points out that very many salts possess six molecules of water of crystallization, and expresses the opinion that this has some connection with the co-ordination number. His attempts to make salts containing more water of crystallization, such as  $\text{ZnSO}_4 + 7\text{H}_2\text{O}$ ,  $\text{MgPtCl}_6 + 12\text{H}_2\text{O}$ , and analogous salts, agree with his theory cannot yet be termed satisfactory. At all events, he has laid great emphasis on the

fact that the number six plays a very important rôle in the groupings occurring in inorganic chemistry. The different dissociation tensions of the different  $\text{H}_2\text{O}$  molecules in salts containing water, *e.g.*  $\text{CuSO}_4 + 5\text{H}_2\text{O}$ , cannot be understood by Werner's theory.

## CHAPTER VIII

### *COMPOSITION OF THE ATOMS. ELECTRONS*

THE study of electrical discharges through gases has led to the opinion that they are enabled to take place by the aid of so-called electrons, small particles which are not greater than the thousandth or two thousandth part of an atom of hydrogen, but carry the same electric charge as that atom, but of opposite sign. It is natural that an attempt has been made to explain matter as built up of these electrons. In this way the hypothesis of Prout has been, so to say, revived, with the difference that, instead of hydrogen atoms, these electrons—1000 or 2000 times smaller than the hydrogen atoms—have been assumed as ultimate particles.

This opinion has attained a certain degree of probability through the research of Lenard<sup>1</sup> on the absorption of so-called cathode rays by different materials. The cathode rays are nothing but electrons endowed with a high speed of motion, that sometimes approaches to the velocity of light ( $3 \times 10^{10}$  cm. per second). Lenard made his experiments with a tube, AB (see Fig. 12), containing a high vacuum, in which he produced

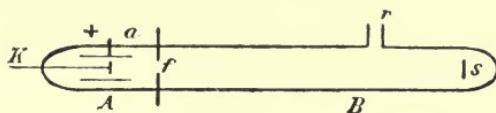


FIG. 12.—Kathode ray tube (Lenard).

cathode rays by sending an electric current between the cylindrical anode *a* and the plane cathode K. The cathode rays were emitted perpendicularly to the plane end of K, and

<sup>1</sup> Lenard, *Ann. Physik. u. Chem.* (3), 1895, **56**, 255; (4), 1903, **12**, 714. Cf. also Becker, *Ann. Physik.* (4), 1905, **17**, 8.

passed through a small "window" of thin aluminium plate, *f*, so that they proceeded along the axis of the tube AB. This tube could be filled through the side tube *r* with gases at different pressures. The strength of the cathode rays was measured by taking advantage of their property of producing a spot of phosphorescent light on a prepared screen, *s*, which could be placed at different distances from *f*. Not only could the absorption of cathode rays by different gases be measured in this way, but also that exerted by thin plates of solid bodies, such as glass, mica, and metals placed near *f*. The great discovery of Lenard consisted in his demonstration of the fact that cathode rays of high velocity—about  $10^{10}$  cm. per second—are absorbed to the same extent by the same quantity of matter, whether this consist of atoms of gases, as hydrogen or oxygen, or of atoms of metals or glass in the solid state. This fact may easily be understood if we suppose that matter is composed of electrons, and that the same quantity (weight) of matter always consists of the same number of electrons, which are arranged in different ways in the different materials. If the speed of the cathode rays decreases, then the influence of different materials becomes different. This depends probably on the position of the electric charges on the atoms, which are able to cause a sensible deviation of the electrically charged cathode rays, if their velocity is not exceedingly high.

Lenard calculated the rate of absorption in the following manner. If a radiation of the intensity  $I_0$  falls upon an absorbing layer of  $d$  cm. thickness, and having the absorption-coefficient  $a$ , then the intensity of the radiation  $I$  on the other side of the plate is—

$$I = I_0 e^{-ad}$$

and the absorption-coefficient, if  $I$  and  $I_0$  are measured, is found to be—

$$a = \left( \log_e \frac{I_0}{I} \right) \frac{1}{d}$$

Using this formula, Lenard calculated the following absorption-coefficients  $a$  for cathode rays possessing a velocity of  $10^{10}$  cm. per second ( $= \frac{1}{3}$  velocity of light), in a medium of density  $\delta$ :

		$a$	$\delta$	$\frac{a}{\delta}$
Hydrogen gas, pressure, 3·3 mm. Hg.	.	0·00149	0·000000368	4040
Air	0·78 "	0·00416	0·00000125	3330
Hydrogen	760 "	0·476	0·0000849	5610
Air	760 "	3·42	0·00123	2780
Sulphur dioxide	760 "	8·51	0·00271	3110
Thin sheets of collodion, weight sq. cm. = 1·64 mg.		3,310	1·10	3010
Paper	2·05 "	2,690	1·30	2070
Glass	1·75 "	7,810	2·47	3100
Mica	3·16 "	7,250	2·80	2590
Aluminium (thickness 0·003 – 0·03 mm.)	.	7,150	2·70	2650
Brass (thickness 0·0003 – 0·0028 mm.)	.	23,800	8·90	2670
Silver ( 0·00018 – 0·0021 mm.)	.	32,200	10·5	3070
Gold ( 0·00065 – 0·00196 mm.)	.	55,600	19·3	2860

The mean value of  $\frac{a}{\delta}$  is 3200. From this hydrogen only is a noteworthy exception. The observed differences may depend upon the velocity of the cathode rays not being high enough. The absorption-coefficient alters considerably with this velocity, as is seen from the following table, in which Lenard has included the measurements of R. T. Strutt<sup>1</sup> on the  $\beta$ -rays from radium, which are identical with cathode rays of a very high velocity, closely approximating to that of light:—

#### ABSORPTION-COEFFICIENT FOR CATHODE RAYS OF GASES AT 1 MM. PRESSURE.

Velocity of the cathode rays.	Hydrogen.	Atm. air.	Argon.	Carbon dioxide.
$1 \cdot 1 \times 10^8$ cm. sec.	44·0	30·0	28·0	34·0
$2 \cdot 5 \times 10^8$ "	14·6	27·0	26·0	32·0
$4 \cdot 3 \times 10^8$ "	6·0	21·0	20·0	28·0
$15 \cdot 0 \times 10^8$ "	1·2	3·9	4·2	7·0
$30 \cdot 0 \times 10^8$ "	0·19	0·85	1·3	2·0
$100 \cdot 0 \times 10^8$ "	0·00062	0·0050	—	0·0067
$300 \cdot 0 \times 10^8$ "	0·0000006	0·000009	0·00001	0·00001

<sup>1</sup> Strutt, *Nature*, 1900, 61, 539.

Hydrogen, which, at high velocities, shows the least absorption for cathode rays—in agreement with its low density—behaves in the opposite way at low velocities of the cathode rays.

The circumstance that a cathode ray may pass through leaves of metal up to 0·03 mm. thickness shows that the electrons may travel through thousands of molecules. There must, therefore, exist very great interstices between the electrons of which a metal molecule is built up.

Now, by definition the absorption-coefficient is a measure of the sum of the cross-sections of all the obstructing particles in 1 c.c. The circumstance that the absorption-coefficient increases very rapidly as the speed of the electrons decreases, is regarded by Lenard as a consequence of the deviating effect of their electric charges on the paths of the electrons. The true cross-section of the electrons must be the lower limit to which the absorption-coefficient decreases, as the velocity of the impinging cathode rays approaches the velocity of light (a higher speed is theoretically impossible). Therefore the sum of the cross-sections of all the electrons in 1 c.c. of hydrogen gas at 1 mm. pressure must be less than 0·0000006 sq. cm. According to the kinetic theory of gases, the sum of the cross-sections of the hydrogen molecules in the same case is 13 sq. cm. If we now suppose that there are  $N$  hydrogen molecules in 1 c.c. gas at 1 mm. pressure, the sum of their cross-sections is  $Q = N\pi R^2$ , where  $R$  is the radius of the hydrogen molecule. Further, if every molecule of hydrogen contains 2000 electrons, each of radius  $r$ , the sum of their cross-sections must be  $q = 2000N\pi r^2$ . Now, the ratio of  $q : Q$  is about 0·0000006 : 13, and is also equal to the ratio  $2000r^2 : R^2$ . According to the kinetic theory of gases,  $R$  is about  $0·2 \times 10^{-7}$  cm. Consequently we have—

$$2000r^2 : (0·2 \times 10^{-7})^2 = 6 \times 10^{-7} : 13$$

from which we find  $r = 0·961 \times 10^{-13}$  cm., i.e. approximately  $10^{-13}$  cm. The volume of the electrons in a molecule of hydrogen is only a small fraction of the volume of the molecule itself, namely  $\frac{2000 \times (10^{-13})^3}{(0·2 \times 10^{-7})^3} = 2·5 \times 10^{-13}$ , i.e. less than the billionth part.

Hydrogen gas at 1 mm. pressure has the density 0·00000011; if it were condensed 200 million times, a substance of about the

density of platinum would be obtained. The volume of the electrons in a cube of 1 m. side (1,000,000 c.c.) of this substance would be only about 20 c.c. The molecules of platinum fill up about 0·4 of the space.

We have supposed above that the molecular distance is about  $10^{-8}$  cm. This magnitude may also be determined electrically. If we use a low electromotive force to decompose acidulated water, we get a rapidly decreasing current, a so-called charging current. The one electrode, the negative one, may be a plate of platinum, the other a so-called unpolarizable electrode. The current drives hydrogen ions to the platinum electrode; they are not discharged, however, but remain at a certain distance from the cathode. This system may then be regarded as a Leyden jar. The capacity of this Leyden jar is defined as the ratio of the quantity of the electricity which was passed through the cell to the applied electromotive force.

Now the capacity of a Leyden jar may be calculated from its superficial area and the distance apart of its two charged plates. In this case the plates are the platinum cathode and the layer of hydrogen. The nearer these are to each other, the greater is the capacity. Helmholtz<sup>1</sup> determined in this way the distance between the cathode and the hydrogen layer, and found it to be  $10^{-8}$  cm. Other determinations have been made since, and found to agree with those of Helmholtz. We have assumed this value in the calculations given above.

J. J. Thomson,<sup>2</sup> who has carried out excellent work on the nature of cathode rays, is at present engaged in working out an hypothesis on the composition of atoms. He imagines an electrically neutral atom to be composed of a great number of electrons, the number being proportional to the weight of the atom. As these electrons carry a very great charge of negative electricity, it is necessary to further suppose that the atom, being electrically neutral, contains just the same quantity of positive electricity; this quantity J. J. Thomson supposes to be uniformly distributed over the inside of a spherical shell, which may be regarded as the limiting surface of the atom. The electrons are supposed to

<sup>1</sup> Helmholtz, *Ann. Physik. u. Chem.* (3), 1879, 7, 337; "Wiss. Abhandlungen," vol. i. p. 855.

<sup>2</sup> Thomson, *Phil. Mag.* (6), 1904, 7, 237.

move in circles round the centre of the atom, and are therefore driven outwards by a definite centrifugal force. Furthermore, they are subjected to the mutual repulsion of their negative charges and to the attraction of the total positive charge. Thomson has solved the problem for the special case in which the electrons are arranged in circles around the centre of the atom. He calculates that the highest number of electrons which can move in a single circle round a common centre is five. If there are six electrons moving in one and the same circle, their motion is unstable, whatever may be the velocity, and the electrons therefore arrange themselves so that one of them goes to the centre and the remaining five move in the same circle. With a great number of electrons it is necessary to suppose them placed on several different circles ; thus, for instance, if their number is 60, the electrons move round five different circles, 20 on the outermost circle, 16 on the next, 13 on the third, 8 on the fourth, and 3 on the innermost circle.

The stability of the outermost ring increases with the number of electrons within it. If the outermost ring is not very stable, it may, even under the influence of rather weak external forces, lose one of its electrons, and then we have a positively charged atom with the unit atomic charge. This represents a monovalent positive ion, such as the hydrogen ion. In the same way, we may figure to ourselves the genesis of divalent ions, such as the calcium or the zinc ion ; of trivalent ions, such as the aluminium ion ; and so forth.

In this way we get a good representation of the changing valencies of the atoms, so that, for instance, we can easily imagine the indium atoms to be mono-, di-, and tri-valent. But it is difficult to understand why the trivalent indium atom should be the most stable of the three, as experiment shows, and also why the valency in most cases varies by even and not by odd numbers.

When the stability of the outer ring gets very great—there being a relatively large number of electrons inside it—it may be possible for one or more electrons to be on the surface of the atom without breaking up the ring ; in this case the atom would carry a charge of negative electricity, and would then behave like a negative ion. According to the number of negative

electrons on its outside, it would be mono-, di-, tri-, tetravalent, and so on.

The weights of the ions would not sensibly differ from those of the corresponding atoms; for if the weight of one electron is only the two-thousandth part of that of an atom of hydrogen, the loss of one electron from the hydrogen atom would only cause a decrease in weight of one two-thousandth. Other atoms have a much greater weight than that of hydrogen, and therefore the loss of an electron would be still less perceptible.

The unit of matter represented by the electron is so exceedingly small compared with the quantity of matter in the atoms, that it is altogether impossible to decide if Lenard's modification of Prout's hypothesis is true, by making determinations of atomic weights; for if these attain the highest possible degree of accuracy, they will still be far from exact enough to come within the limit of the two-thousandth part of the present unit, which corresponds approximately to the atomic weight of hydrogen.

It seems rather difficult to explain, according to Thomson's deductions, how an atom may sometimes behave as a negative ion, and sometimes as a positive ion, as Berzelius supposed for nitrogen and Faraday for sulphur. It is also difficult to develop the ideas of Thomson so as to obtain a satisfactory representation of such a case as that of nitrogen in sal-ammoniac,  $\text{NH}_4\text{Cl}$ , where the nitrogen atom seems to bind four positive atoms ( $4\text{H}$ ) and one negative atom ( $\text{Cl}$ ).

In such a compound as  $\text{HCl}$  the molecule consists of one atom of hydrogen, which has lost an electron, and one atom of chlorine, which has added an electron on to its external surface. Therefore the weight of such an electrolyte is just as great as if both its components consisted of whole atoms.

With the help of his ideas on the composition of matter, Thomson also endeavours to give an explanation of the so-called Mendeléeff's system of the elements.

This system represents, as is well known, very many of the chemical and physical properties of the chemical elements. Mendeléeff's latest formulation of his system is as follows (Prometheus, 15, 97-102, 121-125, 129-134, 145-151: 1903):—

## PERIODIC SYSTEM OF THE ELEMENTS ACCORDING TO MENDELÉEFF.

Series.	Group 0.		Group 1.		Group 2.		Group 3.		Group 4.		Group 5.		Group 6.		Group 7.		Group 8.	
	X	Y	H	Li	Be	Mg	Al	C	Si	N	P	O	S	Cl	F	Co	Ni	(Cu)
1			1.008															
2	He	4.0	Li	7.03	Na	23.05												
3		Ne	19.9	K	39.1	Ca	40.1											
4	Ar	38		Cu	63.6	Sr	87.6											
5			Rb	85.4	Ag	107.9	Cd	89.0	In	90.6	Zr	94.0	Nb	96.0	Te	I	(Ag)	
6	Kr	81.8					112.4									127	127	
7				Cs	132.9	Ba	137.4	La	139	Ce	140	—	—	—	—	—	—	
8	Xe	128					—	—	—	—	—	—	—	—	W	184		
9															Ta	183		
10		—													Bi	208		
11															Pb	206.9		
12		—													Th	232		
															U	239		

This scheme differs from its old classical form by the addition of the new elements contained in atmospheric air, for a knowledge of which we are indebted to the epoch-making researches of Sir William Ramsay. As these elements have hitherto shown no "affinity" to any known element, they are placed in a special group 0, containing the elements without valency.<sup>1</sup> (The group 1 is composed of the elements with the valency 1, and so on.) Further, Mendeléeff introduces two new elements, X and Y, each with less atomic weight than that of hydrogen. Both of these would belong to the group 0, and we should, therefore, be inclined to search for them in the gases of the atmosphere. Now, before helium was known as a terrestrial element, a well-defined spectral line of the wave-length  $587\cdot5 \mu\mu$  was known in the spectrum of the sun's highest atmosphere (in the protuberances, and above the sunspots), which was not found in the spectrum of any substance of terrestrial origin. The physicists, therefore, supposed that in the sun's atmosphere there existed an unknown elementary gas, to which the name helium (*i.e.* sun-element) was given. This prediction of a new element was brilliantly verified by the discovery of helium in various uranium minerals by Ramsay. It has been since shown that other spectral lines of the sun and different stars belong to the spectrum of this substance. Further, the other new elements of the earth's atmosphere are represented in the sun's highest atmosphere, as evidenced by characteristic spectral lines.

Hence, although we do not know the element Y in the earth's atmosphere, we may search for it in that of the sun. Indeed this contains an element, called coronium, since it is characteristic of the sun's corona, which is not known to occur on the earth. Perhaps, says Mendeléeff, coronium is identical with the element Y sought for. This coronium ( $531\cdot6 \mu\mu$ ) is contained in higher layers of the sun's atmosphere than those containing hydrogen and helium, the lightest elements known; and it might, therefore, be supposed to have a lower molecular weight than these, just as would be expected for the element Y.

<sup>1</sup> There are a number of different modifications of Mendeléeff's arrangement of the elements, as, for instance, those of Abegg, Ramsay, etc. They present different advantages and also disadvantages, so that there is no special reason why they should be preferred to that of Mendeléeff.

From the different regularities in the atomic weights and the positions of the elements in his scheme, Mendeléeff calculates the atomic weight of the element Y to be 0·4, or probably somewhat less. As it belongs to the group 0, it will, like the other elements of this group, consist of monatomic molecules, and its relative density (the density of hydrogen = 1) is therefore only 0·2, or still less. The other element X ought also to belong to the group 0, and to be a gas still lighter than the element Y. The element X is called Newtonium, in honour of the immortal physicist. From very bold theoretical considerations, Mendeléeff calculates its atomic weight to be about 0·000001. Its atoms ought, therefore, to be about 500 times lighter than the electrons. As a matter of fact, the calculation of Mendeléeff could just as well have led to a number equal to, or greater than, 0·0005 (corresponding to the electron), as we shall see further on. Mendeléeff supposes this element to form the substance of which the luminiferous ether is built up.

This is not the place to enter upon the many great difficulties connected with this idea, especially the explanation of the transverse vibrations of the luminiferous ether, which are inconsistent with the nature of an extremely attenuated gas. Nor shall we discuss the weak points of Mendeléeff's scheme in respect to the known elements, as these imperfections are well known to every chemist.

A short account, however, may be given of the manner in which J. J. Thomson seeks to reconstruct this scheme by the aid of the known properties of the electrons.

We may, with Thomson, consider the elements of one series, for instance, series 3—

Elements	Ne	Na	Mg	Al	Si	P	S	Cl
At wt.	19·9	23·05	24·1	27·0	28·4	31·0	32·06	35·45
Diff.	3·15	1·05	2·9	1·4	2·6	1·06	3·39	

and compare this series with the possible combinations of electrons, containing an outer ring of 20 electrons. These and their nearest neighbours are, according to Thomson, the following:—

19	20	20	20	20	20	20	20	20	20	21
16	16	16	16	17	17	17	17	17	17	17
13	13	13	13	13	13	13	14	14	15	15
8	8	8	9	9	10	10	10	10	10	10
2	2	3	3	3	3	4	4	5	5	5
<hr/>										
58	59	60	61	62	63	64	65	66	67	68

Of these, the system of 59 electrons contains in its outermost ring the greatest possible number of electrons that may be held together by the inner electrons. Therefore this combination is very unstable, and easily loses one electron, thereby becoming the combination 58 with a unit positive charge. On the other hand, the compound of 58 electrons is so stable in the outer ring that it very easily adds on a negative electron and holds it at the surface of the atom. That is, as soon as the combination of 59 electrons has been transformed into the atom with 58 electrons, it will again bind one electron, so that the whole process consists in the transference of one electron of the 59 to the outside of the atom. This atom will, therefore, possess neither a positive nor a negative charge; it will be without valency, and therefore belong to the group 0.

The outside electron of the atom ( $58 + 1$ ) may, on the other hand, again go back to the outer ring, so that the atom 59 is reformed. There will therefore be an equilibrium between uncharged 59-atoms and positively charged ( $58 + 1$ )-atoms with an outer negative electron. But in both cases the total charge is zero, and we have an element of the group 0, like neon, before us. In an analogous way Thomson tries to demonstrate that the 67-atom represents an element of the group 0, like argon.

If we then proceed to the 60-atom, we find that it may lose one electron, and thus be transformed into the 59-atom; but if it loses one electron more (58-atom), it will add it on to its outside again, just as the 59-atom did. The 59-atom derived from the original 60-atom, therefore, represents a monovalent positive element, like sodium.

By extending this reasoning to the 61-atom, we find that it may lose two electrons and behave as a divalent positive atom, like magnesium; the 62-atom will give a trivalent positive atom, like aluminium; the 63-atom a tetravalent positive atom, like silicon (in chloride of silicon,  $\text{SiCl}_4$ ); and the 64-atom a pentavalent atom like the phosphorus atom (in  $\text{PCl}_5$ ); and so forth.

On the other hand, by adding negative electrons to the outside of each, the 66-, 65-, 64-, and 63-atoms will be converted into negatively charged mono-, di-, tri- and tetra-valent negative atoms, corresponding to chlorine, sulphur, phosphorus, or silicon in their compounds with positive hydrogen and its substituents.

This representation of Mendeléeff's system is very interesting, and it may be hoped that with further work success will meet the efforts to remove the numerous difficulties with which it has now to contend. One of these difficulties is inherent to the scheme itself; the atomic weight ought to increase with the positive valency in every series. This seems not to be the case. There are two very prominent exceptions to this rule: The one is argon, which has a higher atomic weight than potassium (39.8 against 39.1). The figure 38 for argon given by Mendeléeff is only a "theoretical" value, computed in order to retain the simplicity of his scheme; the experiments of Ramsay<sup>1</sup> give 39.8 for argon, and potassium has been very accurately determined to be 39.1. The other exception is met with in the case of the two elements tellurium and iodine, with the atomic weights 127.6 and 126.97 respectively.

This difficulty is only a specially striking instance of a more general one; the systems in Thomson's series differ from each other by one electron, so that the difference between two consecutive atomic weights is constant. This does not agree with the much more complicated behaviour of the natural elements. In the series 2 this difference varies between 1.05 and 3.39, *i.e.* in the proportion 1 : 3.2, in a somewhat irregular manner. In other series this variation is of the same order.

But there are other difficulties not specially characteristic of Mendeléeff's scheme itself, but only of its representation by Thomson. After the second series with 20 electrons in the outer

<sup>1</sup> Ramsay and Travers, *Proc. Roy. Soc.*, 1898, **64**, 183.

ring, there will come a series with 21 electrons in this ring, then one with 22 electrons, and so on. These series correspond to the series 3, 4, 5, 6, etc., in Mendeléeff's scheme. Now, the number of atoms belonging to one series is very nearly constant, and likewise the difference between the atomic weights of the extreme elements is not very unlike in succeeding series. The series of Thomson behave in quite another way. It is only by chance that the series with 20 electrons in the outer ring contains 7 elements with valencies corresponding to the second, third, or seventh series of Mendeléeff. In general, the number of elements belonging to a Thomson's series will increase nearly proportionally to the  $\frac{2}{3}$  power of the atomic weight of its first element; therefore the number of elements in the seventh series ought to be about three times as great as that in the third series and about eight times as great as that in the second series. Thomson's scheme would, therefore, if it were worked out, differ considerably from its prototype.

One might imagine that perhaps this difficulty would disappear if the atoms were represented, not by rings of electrons lying parallel to one another, but by some other arrangement of the electrons, which would correspond better with the three-dimensional configuration of the atoms. But, as Thomson remarks, the general outlines of his system would not be substantially altered by such a modification.

Another difficulty, and perhaps the greatest one, is that experiment shows that the mass of the electrons is only about the two-thousandth part of that of the hydrogen atom. According to this idea, it would be natural to suppose that the neon atom consists of 39,800 electrons, the sodium atom of 46,100. It would, therefore, not be one step from neon to sodium, but 6300. Hence it will be necessary to add to Thomson's scheme the supposition that not one electron, but a great number of electrons, together with the corresponding quantity of positive electricity, makes the difference between two consecutive elements. And as the differences between the atomic weights of consecutive elements are not at all constant, it will be necessary to assume that the complex of electrons is very different in different cases. By this amendment the Thomson scheme loses its simplicity, and at the same time much of its theoretical value.

The latest calculations of J. J. Thomson<sup>1</sup> may perhaps open out a new perspective. They are based on three different series of measurements, and lead to the result that "the number of electrons (corpuscles) in an atom of an elementary substance is of the same order as the atomic weight of the substance." Thus, for instance, the scattering of Röntgen rays by air gave the result that the number of electrons in a molecule of air is about 25 (according to experiments of Barkla), whereas the mean molecular weight of air is 29. This result reminds one very much of the hypothesis of Prout.

Another objection may be made to Thomson's scheme, because it demands that there should be two elements of the group 0 in every series. Thus, in series 3, neon should correspond both to the 58-atom and to that composed of 59 electrons. We know nothing of such a duplication of the elements of group 0. Further, if, for instance, the 59-atom is unstable and loses one of its electrons, why should it regain its stability by simply adding on the lost electron to its outside, and not just as well by attracting a negative monovalent atom, *e.g.* a chlorine ion? In this manner the positive potassium ions unite with negative chlorine ions and give salt molecules. One cannot ignore the fact that it seems necessary to find the reason why the 59-atom does not behave in the same way in order to acquire stability; in other words, why the 59-atom cannot as well be a monovalent positive element as one without valency.

It is very interesting to note that at the same time as Thomson worked out his idea of the composition of matter, the Japanese physicist Nagaoka<sup>2</sup> was also led to similar assumptions in order to explain the optical, especially the spectral, phenomena of matter. He supposes electrons to move in concentric rings around a positively charged centre; also that the whole positive charge is concentrated at one point, and not equally distributed over a sphere. Nagaoka, as well as Thomson, has worked out an explanation of the breaking down of the radium atom into helium and something else. If this breaking down is finally satisfactorily proved, these theoretical deductions may prove of value.

<sup>1</sup> J. J. Thomson, *Phil. Mag.* (6), 1906, **11**, 769.

<sup>2</sup> Nagaoka, *Nature*, 1904, **69**, 392.

Lenard<sup>1</sup> has put forward the idea that in the spectrum of a metal, *e.g.* Na, which can be resolved into a principal and several subsidiary series, the principal series corresponds to the vibrations of the neutral atom, and the first, second, etc., subsidiary series to the vibrations of the metal atoms which have lost 1, 2, etc., electrons. It is possible that this hypothesis will be of great value in the elucidation of complicated spectra.

Lenard has shown that in the arc light the principal series (of Li and Na) is developed in the outermost edge of the arc, the first subsidiary series in a zone which lies within this edge, the second subsidiary series in a zone which lies still more towards the centre, and so on. Since there is no doubt that the temperature increases towards the centre, this would indicate, according to the second law of thermodynamics, that the splitting off of the electrons is accompanied by loss of heat, which is just the opposite to the behaviour of radium. Accordingly Na must become divalent at higher temperatures, trivalent at still higher, and so on. It would, perhaps, be more in accordance with the stability of the monovalent Na ion to assume that the principal series owes its existence to this ion, the first subsidiary series to the divalent Na ion, and so on. In any case, Lenard's idea seems to be preferable to that of Thomson's.

According to the investigations of Stark,<sup>2</sup> the uncharged atoms produce band spectra, while the monovalent ions of H, Na, and K, give the principal series and the first subsidiary series of the line spectrum. Using Doppler's principle, he measured the velocity of the ions in question under the influence of a definite fall in potential. A continuation of these interesting investigations seems very promising.

The views developed by Rutherford, Soddy and Ramsay are based upon a stronger experimental evidence than the theoretical deductions of J. J. Thomson, and merit a high interest. It seems rather probable, from the researches on radio-active substances, that these are subjected to steady changes which go on with different velocities. These velocities are characterized by the time necessary for the decomposition of half of the original

<sup>1</sup> Lenard, *Ann. Physik.*, 1905, **17**, 227.

<sup>2</sup> Stark, *Göttinger Nachrichten Math.-phys. Kl.*, 1905, 459.

quantity of radio-active substance. For instance, according to Rutherford,<sup>1</sup> radium is decomposed in 1300 years. The first product is a gas, radium emanation, which in four days gives a deposit called radium A. This, however, gives radium B in 3 minutes, which in 21 minutes changes to radium C, and this, in its turn, gives radium D in 28 minutes (all the times correspond to a decomposition of 50%). These substances are all solid, and produce radium E in about forty years, which changes to radium F in six days. Radium F is probably identical with polonium, and loses 50% of its radioactivity in 143 days, giving an inactive substance. Whether the process is complete after these eight changes we do not know.

During these transformations  $\alpha$ - $\beta$ -, and  $\gamma$ -rays are given off according to the following scheme, which is easily understood:—

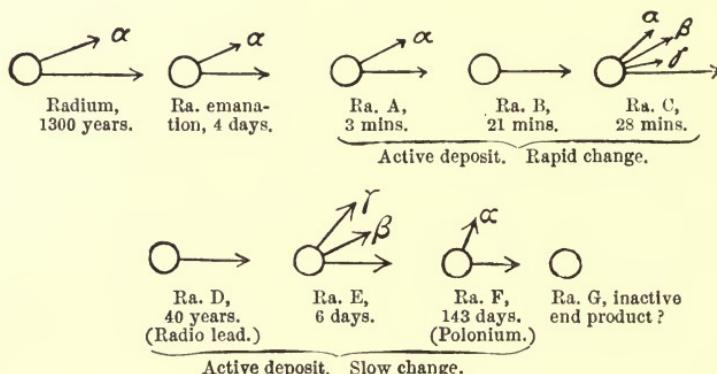


FIG. 13.—Transformations of radium, according to Rutherford.

Now, we imagine that the  $\beta$ -rays correspond to the expulsion of negatively charged electrons with the velocity of light, whereas the  $\alpha$ -rays consist of positively charged atoms—since helium seems to be produced during the radiation, Rutherford assumes them to be helium atoms—possessing, according to him, a speed of  $2.5 \times 10^9 \frac{\text{cm.}}{\text{sec.}}$ , the twelfth part of that of light. Rutherford holds the opinion that every change accompanied by  $\alpha$ -rays is characterized by the loss of one atom of helium, so that finally the radium atom would lose five helium atoms, and therefore the (end-) product Ra. G would have an

<sup>1</sup> Rutherford, "Radio-activity," 2nd edit. Cambridge: 1905, p. 450.

atomic weight of  $225 - 5 \times 4 = 205$  ( $\text{He} = 4$  being the atomic weight of helium). The emission of  $\gamma$ -rays, which are of the same kind as Röntgen rays, causes no loss of matter, and the quantity of matter accompanying the radiation of  $\beta$ -rays may be neglected compared with that characteristic for the  $\alpha$ -rays. The energy given out by radium, corresponding to about 100 gram-calories per hour per gram of radium, is supposed to correspond to the emission of  $\alpha$ -particles, each possessing a kinetic energy of  $5.9 \times 10^{-6}$  erg. In the present case the processes 6 to 8 go on so slowly that they may be neglected during the short time which has elapsed since the preparation of the radium.

From these figures, and assuming that 1 c.c. of hydrogen at  $0^\circ$  and 760 mm. contains  $3.6 \times 10^{18}$  molecules, Rutherford calculates that about  $18.9 \times 10^{10}$   $\alpha$ -particles are ejected from one gram of radium per second, i.e.  $4.7 \times 10^{10}$  particles per second for each of the four processes, and that one gram of radium contains  $36 \times 10^{21}$  atoms, its atomic weight being 225. Other measurements, which depend on the radio-activity of, and the evolution of helium from, radium bromide, lead Rutherford to the result that each gram of radium sends out  $4 \times 6.2 \times 10^{10}$   $\alpha$ -particles per second. From this number, which he thinks more correct than the one given above, it follows that in one second  $1.75 \times 10^{-11}$  grams, and in one year  $5.53 \times 10^{-4}$  grams, undergo transformation in every gram of radium, corresponding to a change of 50% in 1250 years.

The two active substances thorium and uranium possess an activity about two million times less than that of radium, as measured by their property of discharging a charged electroscope. During their successive transformations the radium and thorium preparations emit four  $\alpha$ -rays, whereas the uranium preparations only expel one. The number of molecules transformed in unit time is proportional to the number of  $\alpha$ -rays emitted during every change; hence the "life" of a radio-active atom is inversely proportional to the radio-activity and directly proportional to the number of emitted  $\alpha$ -rays. From these considerations Rutherford calculates that the times necessary for the transformation of 50% of thorium and uranium are  $\frac{1}{4} \times 2 \times 10^6 \times 1250 = 6 \times 10^8$  and  $2 \times 10^6 \times 1250 = 25 \times 10^8$  years respectively.

If radium is a product of decomposition of these elements it is easy to calculate how much radium should be produced in one year. Soddy<sup>1</sup> found that the observed value was not the five-hundredth part of that calculated in the case of uranium.

According to these ideas, radium may be regarded as a composite metal, something analogous to ammonium,  $\text{NH}_4$ . Metallic  $\text{NH}_4$ , alloyed with mercury, was prepared by Berzelius. By the loss of one H it gives ammonia gas, corresponding to the emanation of radium,<sup>2</sup> and by the further loss of an atom of H, diamide  $(\text{NH}_2)_2$ , the mother substance of the hydrazines, discovered by Emil Fischer. By further loss of hydrogen  $\text{N}_2\text{H}_4$  would give  $\text{N}_2\text{H}_2$ , which compound is not known except in the form of its hydroxyl derivative  $\text{N}_2(\text{OH})_2$ , hyponitrous acid. By still further loss of hydrogen, hydrazoic acid,  $\text{N}_3\text{H}$ , and finally pure nitrogen are obtained. It is quite possible that other compounds of hydrogen and nitrogen, intermediate in composition to those given above, may exist. We thus have an analogy between the degradation products of ammonium under loss of hydrogen, and those of radium under loss of helium.

Efforts have also lately been made to explain matter as being only a manifestation of electrical forces. If an electron possessing a certain velocity moves through space, the motion is connected with two kinds of energy: the kinetic energy of the electron's mass and the electromagnetic energy of the surrounding magnetic field. Suppose, now, that the velocity of the motion increases, then both forms of energy increase proportionally so long as the velocity remains much below the speed of light. But as the velocity of the electron approaches this speed the magnetic energy increases more rapidly than the kinetic, and would, if this speed were attained, become infinite; therefore the electron can never have the velocity of light. Hence, there is no longer proportionality between the two kinds of energy for very great velocities of the electrons, but the magnetic energy becomes a continually increasing fraction of the total energy.

<sup>1</sup> Soddy, *Phil. Mag.*, 1905, **9**, 768. Cf. also pp. 19, 20.

<sup>2</sup> Concerning the electrochemical affinity of ammonium, cf. Coehn, *Zeit. Anorg. Chem.*, 1900, **25**, 430; *Zeit. für Elektrochem.*, 1806, **12**, 609.

If we increase the velocity of any mass, it is necessary to supply energy to it. The greater the amount of the supplied energy, the greater, we say, is the mass of the body in motion. In the case of any moving electron, energy must be supplied not only for the kinetic energy of the mass in motion, but also for the magnetic energy. As both these at the commencement are proportional to one another, we may substitute for the magnetic energy an equivalent increase of the mass of the moving electron, and suppose the total energy to be kinetic. In the same manner we might suppose that there was nothing but magnetic energy, and neglect the mass of the electron. This mass might therefore only be apparent and not real. But if this were true, we might expect that as the speed of the electron approaches the velocity of light its apparent mass would increase beyond all limits. Indeed, some very interesting experiments of Kaufmann<sup>1</sup> seem to indicate such an increase in the apparent mass of the electrons. His figures on the mass of the electrons of  $\beta$ -rays obtained from radium preparations, compared with the calculated values, when the whole mass is supposed to be apparent, *i.e.* electromagnetic, are given below—

Velocity of $\beta$ -rays . . .	2.36	2.48	2.59	2.72	2.83	$\times 10^{10}$
Mass of electrons (observed by Kaufmann)	1.5	1.68	2.01	2.55	3.12	
Mass of electrons (calculated by J. J. Thomson)	1.65	1.83	2.04	2.43	3.09	

The apparent mass of the electron at low speed is put equal to 1. Evidently the figures of Kaufmann show an increase, as Abraham's<sup>2</sup> and J. J. Thomson's<sup>3</sup> calculations require, as the velocity approaches to  $3 \times 10^{10}$ .

Many physicists have expressed themselves in sympathy with the idea that matter is only a manifestation of electrical forces. J. J. Thomson has more than any one else been the skilful advocate of this idea in his remarkable book on

<sup>1</sup> Kaufmann, *Gött. Nachrichten*, 1901, 143; 1902, 291; 1903, 90.

<sup>2</sup> Abraham, *Gött. Nachrichten*, 1902, 20.

<sup>3</sup> J. J. Thomson, "Conduction of Electricity through Gases" (2nd ed.), 1906, 653.

"Electricity and Matter" (1904), to which the reader interested in these questions may be referred.

According to this idea, the mass of a body is not invariable, but will rapidly increase as the velocity of the body approaches to that of light ( $3 \times 10^{10}$  cm. per second). But if the velocity is less than the tenth part of this, the difference in mass from that at very low velocities is insignificant—below 1 %. Now, in reality, if we except the cathode- and  $\beta$ -rays, we never observe matter endowed with such high velocities. The eruptions on the new star in Perseus (February, 1901) did not attain a velocity greater than  $7.5 \times 10^7$  cm. per second, and the greatest observed velocity of the protuberances on the sun is  $8.5 \times 10^7$  cm. per second, exceeding that of our most rapid projectiles by about a thousand times. These velocities are about the four-hundredth part of the speed of light, so that the deviation from the law of the constancy of mass must, even in these extreme cases, have been inappreciable.

Further investigations on these interesting questions seem necessary before these revolutionary ideas will have the chance of being generally accepted.<sup>1</sup>

<sup>1</sup> Cf. above, p. 102.

## CHAPTER IX

### *THEORY OF GASES*

HITHERTO we have chiefly been concerned with the properties of atoms; now we will proceed to consider the properties of molecules.

The great discoveries by which chemistry developed into a science in the modern sense of the word were made during researches on gases. In old times all gases were regarded as a sort of air, and only slowly did observation lead to the knowledge that there exist different gases with very dissimilar properties.

In the seventeenth century, Boyle carried out his fundamental work on gases, and discovered the law that bears his name. He enclosed a quantity of gas in a **U**-tube, of which the one leg was open, the other closed. The gas was confined by means of mercury poured into the open limb. On increasing the pressure by adding more mercury, the volume of the gas decreased. Boyle found that the volume was inversely proportional to the pressure, and the mathematical formulation of his law is therefore—

$$v = K \frac{1}{p}, \text{ or } pv = K, \text{ or } p = KC,$$

where  $K$  denotes a constant proportional to the mass of the enclosed gas,  $p$  is the pressure,  $v$  is the volume, and  $C = \frac{1}{v}$ , the inverse value of the volume, may be called the concentration of the gas.

At the beginning of the last century, Gay-Lussac, in determining the dilatation of gases by heat, made a new discovery. He found that all gases have very nearly the same coefficient

of expansion, their volume at constant pressure increasing by the 273rd part of the value at 0° C. for a rise in temperature of 1° C. The mathematical expression of his law is evidently—

$$v = v_0 \left(1 + \frac{1}{273} t\right) = v_0 \frac{T}{273}$$

where  $v_0$  is the volume of the gas at 0° C. and constant pressure,  $t$  is the temperature in degrees Centigrade, and  $T = 273 + t$  is the corresponding absolute temperature. It is also easy to see that the formula—

$$pv = RT, \text{ or } p = RCT$$

where  $R$  is a constant, includes both the laws of Boyle and Gay-Lussac; for on making  $T$  constant we have the law of Boyle, and on making  $p$  constant we get the law of Gay-Lussac.

The law of Boyle is often called Mariotte's law, because Mariotte discovered it seventeen years later, independently of Boyle. Mariotte tested it chiefly for pressures below 760 mm.; Boyle had done it for higher pressure. About forty years before Gay-Lussac, the Parisian professor Charles had studied the thermal dilatation of gases, and enunciated a law similar to that of Gay-Lussac, and hence the law for the dilatation of gases is often called Charles' law.

Gay-Lussac discovered another law during his work on the properties of gases (1805). Volta had constructed an instrument called the "eudiometer" for determining the quantity of oxygen in air. In this instrument hydrogen was added to the enclosed air, and the mixture exploded by electric sparks. In this way water was formed, which then condensed, so that the volume decreased. The decrease in volume was due to the disappearance of the oxygen and an equivalent quantity of hydrogen from the gas-mixture. In order to ascertain the quantity of oxygen, it was evidently necessary to know what fraction of the diminution of volume was due to the disappearance of the oxygen. This fraction was found to be a third, and therefore of the loss of volume one-third was due to the oxygen, and two-thirds to the hydrogen. In other words, water is formed from one volume of oxygen and two volumes of hydrogen. This fact, in

its simplicity, recalls the law of Dalton. Later on, Gay-Lussac proved that simple proportions by volume were found in all other cases which he investigated, and that if a gas were formed by the combination, the volume of this compound was in a simple proportion to the volumes of the gaseous constituents. Ammonia and hydrochloric acid combine in equal volumes; ammonia and carbon dioxide in the volume proportions 2 : 1 and 1 : 1, according to the circumstances; nitrogen and hydrogen in the proportions 1 : 3; sulphur dioxide and oxygen in the proportions 2 : 1; carbon monoxide and oxygen in the proportions 2 : 1. In the last case the carbon dioxide formed occupies the same volume as the carbon monoxide. In the decomposition of ammonia gas, the volume of the compound is found to be double the volume of the combined nitrogen, and two-thirds that of the combined hydrogen. Water in the gaseous state occupies the same volume as the component hydrogen, and double the volume of the component oxygen.

Gay-Lussac showed how it was possible, by means of his law and the known densities of the elementary gases, to calculate the densities of their compounds.

Berzelius understood perfectly the importance of the connection between Gay-Lussac's discovery and Dalton's law, and wrote the following remarkable words to Dalton (1812): " You are quite right that without the atomic hypothesis the theory of multiple proportions is a mystery, and, as far as I know, all results hitherto obtained contribute to the verification of this hypothesis. But I think there are parts in this theory, as developed by you at the present time, which ought to be altered a little. For instance, that part of it which leads you to assert that the experiments of Gay-Lussac on the volumes of combining gases are inexact. I would rather have supposed that these experiments form the most beautiful proof of the probability of the atomic theory."

Dalton sought to demonstrate the erroneousness of Gay-Lussac's measurements; Berzelius used them for the determination of atomic weights. For instance, Dalton supposed an "atom" of water to consist of one atom of hydrogen and one atom of oxygen; but Berzelius asserted that equal volumes contain equal numbers of *atoms*. As the combining volumes of

hydrogen and oxygen were in the proportion 2 : 1, he expressed the idea that an atom of water is composed of two atoms of hydrogen and one atom of oxygen, and he wrote its formula  $H_2O$ , just as we do now. But there arose a difficulty which Berzelius could not overcome. It was observed that one volume of hydrogen and one volume of chlorine combine to produce two volumes of hydrochloric acid. Therefore, according to Berzelius, one atom of hydrogen combines with one atom of chlorine to form two "atoms" of hydrochloric acid. This idea was incompatible with the conception of an "atom," since one atom of hydrogen must then be supposed to be *divided* between the two newly formed "atoms" of hydrochloric acid.

An Italian professor, Avogadro, found a very simple way out of this difficulty. He introduced a new conception—that of the molecule—and supposed that one molecule of hydrogen consists of two atoms of hydrogen, and that, similarly, the chlorine molecule is composed of two chlorine atoms. He asserted that equal volumes of different gases (under the same conditions of temperature and pressure) contain the same number of molecules. One molecule, *i.e.* two atoms, of hydrogen and one molecule, *i.e.* two atoms, of chlorine give two molecules of hydrochloric acid. In the same manner, the facts that one volume = molecule = two atoms of oxygen gas and two volumes = molecules = four atoms of hydrogen give two volumes = molecules of water ( $H_2O$ ), and that one volume = molecule = two atoms of nitrogen and three volumes = molecules = six atoms of hydrogen give two molecules (volumes) of ammonia ( $NH_3$ ), were easily understood.

But a long time elapsed before Avogadro's ideas were accepted. The great development of organic chemistry about the middle of last century, during which a great number of gaseous products (at ordinary or easily reached temperatures) were prepared, first showed clearly the utility of Avogadro's idea. The densities of all these gases could easily be calculated with the help of the new hypothesis if one knew their composition. The results were found to be in agreement with observed values. Thus Avogadro's *hypothesis* really developed into a *law*, which term will be applied to it in what follows.

But some difficulties still remained. It was, for instance,

found that the vapour density of sal-ammoniac (which is a compound of hydrochloric acid and ammonia in equal volumes, and therefore must have the composition  $\text{NH}_4\text{Cl}$  or a multiple of it) is only 1·01, only a little more than half that calculated according to the molecular formula  $\text{NH}_4\text{Cl}$ , viz. 1·84. Such "abnormally" low vapour densities were also found for the compounds  $\text{NH}_4\text{CN}$ ,  $\text{PH}_4\text{Br}$ ,  $\text{PH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{S}$ ,  $\text{NH}_4\text{SH}$ ,  $\text{PCl}_5$ , and  $\text{NH}_4\text{OCONH}_2$ . As early as 1857 Cannizzaro gave the right explanation of this abnormality. St. Claire Deville had at that time published a very remarkable research on the dissociation of different compounds at high temperatures. It seemed, therefore, natural to suppose that these exceptional compounds, at the rather high temperatures at which their vapour densities were determined, were partially decomposed; for instance,  $\text{NH}_4\text{Cl}$  into  $\text{NH}_3$  and  $\text{HCl}$ .

This was shown to be true by experiments carried out by v. Pebal and v. Than. v. Pebal<sup>1</sup> fixed, by means of corks, a glass tube,  $r$ , in the axis of another wide glass tube,  $R$ . In  $r$  an asbestos diaphragm was placed at  $a$ , and above it was laid a piece of sal-ammoniac,  $s$ . A narrow glass tube,  $t$ , led to the top of  $R$  just above the opening of the tube  $r$ , and another narrow glass tube,  $v$ , ended at the lower side of  $a$ .  $R$  was heated close to  $a$ , and air blown in through the tubes  $t$  and  $v$ . The air carried the gases from the upper and lower sides of  $a$  through glass tubes,  $u$  and  $w$ , in which pieces of litmus-paper were placed. Now ammonia,  $\text{NH}_3$ , diffuses more rapidly than hydrochloric acid,  $\text{HCl}$ . If, therefore, the piece of sal-ammoniac  $s$  gives off vapours, which are partially

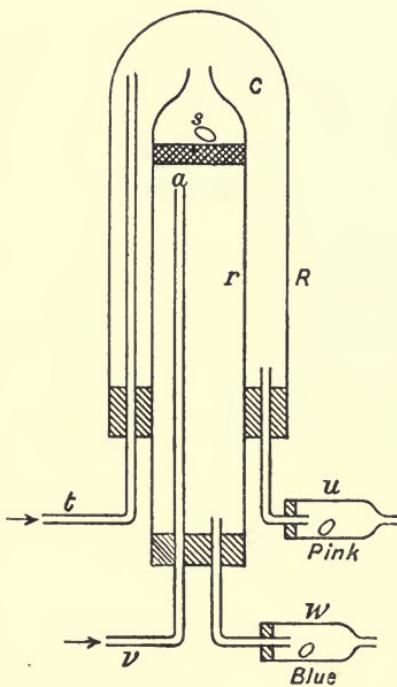


FIG. 14.—Dissociation of sal-ammoniac (v. Pebal).

<sup>1</sup> v. Pebal, *Ann. Chem. u. Pharm.*, 1862, **123**, 199.

decomposed into  $\text{NH}_3$  and  $\text{HCl}$ , we might expect that a greater quantity of  $\text{NH}_3$  will pass through the diaphragm at  $a$ , and therefore the gases blown out through  $w$  should show an alkaline reaction and colour the litmus-paper in  $w$  blue. This was observed to be the case, and likewise the gas remaining above  $s$  showed a deficiency of  $\text{NH}_3$  or an excess of  $\text{HCl}$ , for it coloured the litmus-paper in  $u$  red. If the vapours of sal-ammoniac were not partially dissociated into  $\text{NH}_3$  and  $\text{HCl}$  these observations would be inexplicable.

Nevertheless, the adversaries of this explanation, among whom we find curiously enough the French investigators of dissociation, still continued their opposition to the new ideas. They said that perhaps the asbestos plug at  $a$  might have a chemical influence upon the sal-ammoniac vapour. To overcome this objection, v. Than<sup>1</sup> replaced the asbestos diaphragm by a diaphragm of sal-ammoniac; the result remained the same.

About this time many other researches bearing on this subject were carried out, and they all supported the idea of dissociation. Especially interesting were the determinations of vapour densities over considerable intervals of temperature, by which the increase of the dissociation with temperature was demonstrated. Thus Würtz<sup>2</sup> found the following results for the compound  $\text{C}_5\text{H}_{11}\text{Br}$ , formed from amylene,  $\text{C}_5\text{H}_{10}$ , and hydrobromic acid,  $\text{HBr}$ , which at high temperatures is almost completely dissociated into its two components. (The density of atm. air = 1.)

temp.	155	163	172	185	210	225	237	248	268	295	310	319	360° C.
density	5·27	5·23	5·17	5·13	4·26	4·19	3·83	3·30	3·10	3·09	3·08	2·88	2·61

The formula  $\text{C}_5\text{H}_{11}\text{Br}$  corresponds to the density 5·24, and the mixture in the completely dissociated state to 2·62. From the figures we may therefore conclude that at about 155° C. the molecules of amylene hydrobromide remain intact, and that the dissociation of this compound increases with increasing temperature, till it is complete at about 360° C. Analogous examples are furnished in great number by the more recent investigations on vapour densities.

<sup>1</sup> v. Than, *Ann. Chem. u. Pharm.*, 1864, **131**, 138.

<sup>2</sup> Würtz, *Ann. Chem. u. Pharm.*, 1865, **135**, 314.

We therefore conclude that the law of Avogadro has always led to correct deductions. It was already one of the most important laws of the physics and chemistry of matter, even before van't Hoff enlarged it so as to include the properties of dissolved matter; it is now perhaps the most wide-reaching of all laws.

The analytical expression of Avogadro's law is the same as that of the combined laws of Boyle and Gay-Lussac, namely—

$$pv = RT.$$

$p$ ,  $v$ , and  $T$  have here the same meaning as before, but  $R$  is now a natural constant, the same for all gases, provided that we work with a quantity of gas containing exactly the molecular weight in grams. This quantity is called a gram-molecule, or, more recently, simply a mole. The mole of oxygen, with the molecular weight  $O_2 = 32$ , is 32 grams; that of ammonia, with the molecular weight  $H_3N = 17$ , is 17 grams; and so on. If we express  $p$  in millimetres of mercury, as is usual for barometric pressures, and  $v$  in litres,  $R$  becomes 62·39; if we use the c.g.s. system and express  $p$  in dynes per square centimetre and  $v$  in cubic centimetres,  $R$  has the value  $83\cdot16 \times 10^6$ . Evidently, the dimensions of  $pv$  are now dyne  $\times$  cm., i.e. the dimension of the erg; one erg is  $\frac{1}{418 \times 10^5}$  calories, therefore we may also say that—

$$pv = 83\cdot16 \times 10^6 T \text{ ergs} = 1\cdot99 T \text{ calories.}$$

These three gas laws may easily be deduced from a simple conception of the gaseous state, according to which the gaseous molecules behave as small perfectly elastic hard spheres, moving with great velocities. The consequences of this view are developed in an admirable way in the so-called "kinetic theory of gases." This theory was founded by Daniel Bernoulli in 1738; it was developed to a high degree by Waterston in 1845, and, as his work remained unknown, again by Clausius in 1857. The greatest advances in it were afterwards made by Maxwell and Boltzmann.

The pressure produced on a solid wall by the impact of a perfectly elastic sphere, such as a molecule is imagined to

be, travelling with the speed  $u$ , is  $2 mu$ , if  $m$  is the mass of the moving molecule. If we now imagine one mole, that is,  $M$  grams, containing  $n$  such molecules enclosed in a rectangular vessel of the length  $l$ , the breadth  $b$ , and the depth  $h$ , we may suppose that one-third of the molecules, *i.e.*  $\frac{n}{3}$ , move parallel to the length of the vessel.

These molecules impinge against the end A (see Fig. 15), and then return till they reach the other end B, after which they go back to A again, and so on. If every molecule moves with the velocity  $u$ , the time between the two consecutive impacts against

A will be  $\frac{2l}{u}$ . Therefore in the unit of time (which we will

take to be the second) it gives  $\frac{u}{2l}$  impacts to A. The pressure produced by one impact is  $2mu$ , as shown in theoretical mechanics, and therefore a single molecule, moving parallel to  $l$ , exerts a pressure  $2mu \cdot \frac{u}{2l}$  upon the wall A. Hence  $\frac{n}{3}$  molecules

exert a pressure  $\frac{n}{3} \cdot 2mu \cdot \frac{u}{2l}$ . The end A has an area of  $bh$  sq. cm., therefore the pressure per sq. cm. of A is  $\frac{n}{3} \cdot 2mu \cdot \frac{u}{2l} \cdot \frac{1}{bh} = \frac{1}{3} \frac{nm u^2}{bh}$ .

Now  $bh$  is the volume of the vessel containing the gas, and  $nm$  is the total mass of the enclosed gas, which is assumed to be one mole, *i.e.*  $nm = M$ . Consequently, if the pressure is written  $p$ , we have the formula—

$$pv = \frac{1}{3} Mu^2$$

Now, we know, according to Avogadro's law, that  $pv = RT$ , where  $R = 83.16 \times 10^6$  dynes per sq. cm. Consequently we have—

$$\begin{aligned} \frac{1}{3} Mu^2 &= 83.16 \times 10^6 T \text{ ergs} \\ \text{or } u &= \frac{\sqrt{249.5 \times 10^6 T}}{\sqrt{M}} \text{ cm. per second.} \end{aligned}$$

From this formula we may calculate the velocity of the molecules of a gas. At  $0^\circ \text{ C.}$ , *i.e.*  $T = 273$ , we find for—

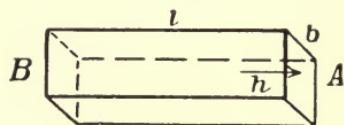


FIG. 15.

Hydrogen, $u = 1837 \frac{\text{m.}}{\text{sec.}}$	Carbon dioxide, $u = 394 \frac{\text{m.}}{\text{sec.}}$
Atm. air, $u = 485 \text{ ,}$	Marsh gas, $u = 651 \text{ ,}$
Oxygen, $u = 461 \text{ ,}$	Ethylene, $u = 493 \text{ ,}$
Nitrogen, $u = 492 \text{ ,}$	Water-vapour, $u = 615 \text{ ,}$
Argon, $u = 424 \text{ ,}$	Ethyl ether, $u = 304 \text{ ,}$

If a gas is placed in a vessel V, in the one wall of which is a small hole, and a vacuum is produced on the outer side P of this wall, the gas-molecules will rush out through the hole o. The number of gas-molecules rushing out in one second is proportional to their velocity, *i.e.* at a given temperature, and for the same number of gas-molecules at the same pressure in V, inversely proportional to the square root of the molecular weight, or of the density of the gas. This was, indeed, found to be true by Graham in 1846, who gave the following figures :—

Gas.	$\sqrt{d}$	Time of efflux.
H <sub>2</sub> . . . . .	0·263	. . 0·276
CH <sub>4</sub> . . . . .	0·745	. . 0·753
C <sub>2</sub> H <sub>4</sub> . . . . .	0·985	. . 0·987
N <sub>2</sub> . . . . .	0·986	. . 0·986
Air . . . . .	1·0	. . 1·0
O <sub>2</sub> . . . . .	1·051	. . 1·053
CO <sub>2</sub> . . . . .	1·237	. . 1·203

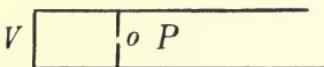


FIG. 16.

The same law also holds good for the velocity of efflux of a gas into a gas-filled space, as has been verified by Bunsen.

As we see from the expression for  $u$ , the molecules have greater velocities at higher temperatures. Suppose that we have one mole of a monatomic gas (that is, a gas the molecules of which consist of single atoms, *e.g.* mercury) enclosed in a vessel of constant volume. Then the quantity of heat supplied to the gas is completely transformed into kinetic energy of the gas-molecules. If the molecules of gas are composed of two or more atoms, a part of the energy supplied may be used up in increasing the distance apart of the atoms against the force of their attraction for each other, or in augmenting their speed of

rotation around their gravitational centre. We will, in the first instance, confine our attention to monatomic molecules. The energy which must be supplied to raise the temperature of one gram of a substance at constant volume through  $1^{\circ}$  C. is called its specific heat at constant volume, and is usually represented by the symbol  $c_v$ . In heating one mole of a monatomic gas from  $0^{\circ}$  C. to the temperature  $t$ , the energy  $Mc_v t$  is consumed, and the speed of the molecules increases from  $u_0$  (at  $0^{\circ}$  C.) to  $u_t$ , the corresponding increase in the kinetic energy being—

$$\frac{1}{2}M(u_t^2 - u_0^2).$$

Therefore we have—

$$Mc_v t = \frac{1}{2}M(u_t^2 - u_0^2).$$

On the other hand, if we heat this same quantity of gas at constant pressure, not only does the kinetic energy of the molecules increase, just as in the former case, but the volume also increases from  $v_0$  to  $v_t = v_0 \left(1 + \frac{t}{273}\right)$ . The work done in overcoming the pressure of the surrounding medium is equal to the product of this pressure and the increase of volume  $v_t - v_0 = v_0 \frac{t}{273}$ . As we are working with one mole, we have—

$$pv_0 = \frac{1}{3}Mu_0^2 \text{ and } pv_t = \frac{1}{3}Mu_t^2,$$

and consequently the work done is—

$$p(v_t - v_0) = \frac{1}{3}M(u_t^2 - u_0^2) = \frac{2}{3}Mc_v t.$$

The specific heat at constant pressure is denoted by  $c_p$ , and the total energy  $E$  supplied is therefore  $Mc_p t$ . This is also equal to the increase in kinetic energy, plus the work done  $p(v_t - v_0)$ . Therefore we have—

$$Mc_p t = Mc_v t + \frac{2}{3}Mc_v t = 1.67 Mc_v t, \\ \text{and } c_p = 1.67 c_v.$$

This relation is found to be in agreement with experiment, as Kundt has shown, in the case of mercury vapour, for which it had previously been deduced by the help of Avogadro's law, and

from chemical evidence, that the molecules were monatomic. This is one of the most startling deductions from the kinetic theory of gases. Later on it was found that  $c_p : c_v = 1.67$  for the rare gases of the atmosphere, which all belong to the group O in Mendeléeff's scheme; therefore these gases are all supposed to be monatomic, so that their atomic weights coincide with their molecular weights. The molecular weights of these gases were determined from their densities according to Avogadro's law, but since they do not form any compounds there was no other means of determining their atomic weights except the determination of the ratio  $c_p : c_v$ .

For all gases other than the monatomic, the ratio  $c_p : c_v$  is less than 1.67, and in general this ratio approaches the nearer to unity, the more atoms there are in the molecule.

Now, the external work done when one mole at constant pressure is heated through  $t^\circ$  is—

$$p(v_t - v_0) = Rt = 1.99t \text{ cal.} = M(c_p - c_v)t.$$

If, therefore, the ratio  $c_p : c_v$  is put equal to  $k$ , we have—

$$(c_p - c_v) : c_v = k - 1, \text{ and } Mc_p = 1.99 \frac{k}{k - 1}.$$

Now, the energy supplied to a gas on heating it  $1^\circ$  C. consists of two parts—the increase in the kinetic energy of the rectilinear motion of the molecules, and the increase in the so-called internal energy of the molecule. The latter consists of the increased speed of rotation of the atoms round their molecular centre, and of the work done in separating the atoms from each other. This internal energy may be called  $U$ . Its increase between the temperatures  $t$  and  $t_0$  is  $U_t - U_0$ .

We have seen that according to Avogadro's law—

$$\frac{1}{2}Mu_t^2 = \frac{3}{2} \times 1.99T \text{ cal.}$$

for all gases. Avogadro's law may also be deduced from the kinetic theory of gases, as Maxwell and Boltzmann have shown, but the deduction is too difficult to be reproduced here. This law says, according to the last formula, that the kinetic energy of the rectilinear motion of the molecules contained in one mole

at the absolute temperature T is the same for all gases, and equal to  $\frac{3}{2} \times 1.99T = 2.985T$ . Further, the external work done in the expansion of one mole at constant pressure, on heating it through  $t^\circ$ , is the same for all gases, and equal to  $1.99t$  cal. For a monatomic gas the energy supplied on heating it at constant pressure through  $t^\circ$  is given by the formula—

$$Mc_p t = (1.99t + 2.985t) = 2.5 \times 1.99t \text{ cal.}$$

For another gas we have—

$$\begin{aligned} Mc_p t &= 2.5 \times 1.99t + U_t - U_0 \\ \text{or } 1.99 \frac{k}{k-1} t &= 2.5 \times 1.99t + U_t - U_0 \end{aligned}$$

From this equation it is easy to find the value of  $U_t - U_0$ , if we know  $k$ . For the diatomic gases N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, CO, NO, HCl, HBr, and HI  $k$  is approximately 1.4, and consequently  $\frac{k}{k-1} = 1.4 : 0.4 = 3.5$ . For these gases, consequently—

$$U_t - U_0 = 1.99t \text{ cal.}$$

or the increase in the internal energy of the molecules is just equal to the external work done.

For the gases Cl<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, ICl, and IBr,  $k$  is about 1.31, and consequently  $\frac{k}{k-1} = 4.23$ . In this case  $U_t - U_0 = 1.73 \times 1.99t$ .

For ammonia and marsh-gas  $k = 1.30$  and  $\frac{k}{k-1} = 4.33$ ,  $U_t - U_0 = 1.83 \times 1.99t$ . For ethyl ether  $k$  is only 1.03, and we find  $U_t - U_0 = 32 \times 1.99t$ .

It is obvious that the internal work is very different for different gases, and increases from 0 for the monatomic gases to very great values (up to 32 times the external work) for gases of complicated structure, such as ethyl ether.

Hitherto we have supposed that all molecules move with the same velocity. Even if we suppose this to be the case at the beginning, the molecules would collide with each other, and according to the laws of mechanics they would have other velocities after impact, so that finally all possible velocities

would be represented. But the mean of the squares of all the velocities would remain the same as the square of the velocity calculated above. Maxwell has calculated the distribution of the different velocities. If a velocity is  $x$ , expressed in terms of the mean velocity as unit, then the number of molecules possessing the velocity  $x$  is proportional to—

$$y = \frac{4}{\sqrt{\pi}} x^2 e^{-x^2}$$

This number is represented by the curve shown in Fig. 17.

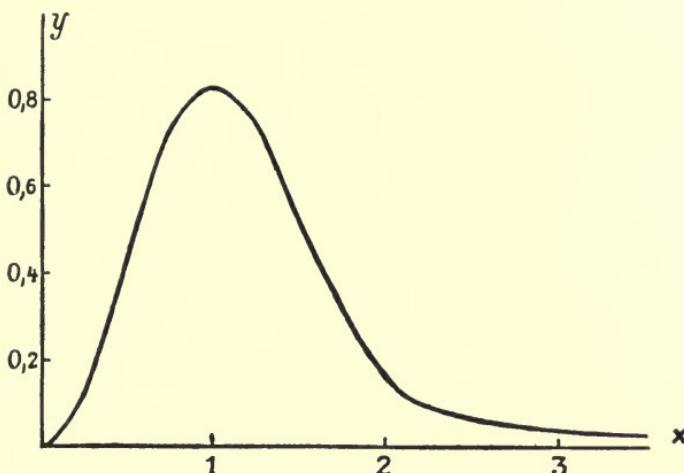


FIG. 17.—Distribution of velocity (according to Maxwell).

We learn from it, that velocities near the mean are the most common, and that very low or very high velocities are rather rare.

The molecules move with these different velocities, and if they had no extension in space they would never collide with each other. The greater the cross-sections of the molecules, the more often will collisions occur, and the less will be the mean path of a molecule between two successive collisions.

Now, there are three phenomena which depend upon the length of the free path of a molecule between two successive collisions, namely, the diffusion of gases into each other, the viscosity of gases, and the conduction of heat through gases.

If the molecules did not collide with each other when moving, they would diffuse with the molecular speed. Thus, for instance, if sulphuretted hydrogen were prepared at the one end of a tube 400 metres long, the smell of it would be observed at the other end of the tube after the lapse of one second. Experience shows that this is by no means the case, and if the sulphuretted hydrogen is not conveyed from one end to the other by means of gas-currents, it will take many years before it can be smelt at 400 metres' distance from the point of production. This depends on the collisions of the molecules of  $H_2S$  with the molecules of the air, and the time for reaching the point 400 metres distant will be the greater, the greater the number of colliding air molecules.

In the same manner, if a gas-current is blown through a narrow tube, the layer of gas molecules nearest to the walls of the tube will remain at rest, because of friction against the tube, and the speed of the moving gas will increase towards the axis. Again, molecules will diffuse from the external slowly moving layers into the central rapidly moving portion of the gas, and will retard its motion. This phenomenon is called internal friction, or viscosity. By measuring it, we are able to form an opinion respecting the length of the mean free path of the molecules, and consequently we obtain an idea of their cross-section.

The third method of measuring these magnitudes is by determining the conductivity of gases for heat. We may imagine a mass of gas in a vertical tube heated at its upper end. The molecules at the upper end will then possess a higher velocity than those below. By diffusion these speedier molecules enter the lower layers, and by collision they increase the motion of the molecules in these layers, so that the heat diffuses from the top to the bottom of the tube. Evidently this diffusion of heat will depend upon the mean free path of the molecules, and therefore it is possible, by experiments on the conduction of heat, as well as by determinations of the rate of diffusion or of the viscosity, to determine the cross-section of the molecules.

The method that has been used is to determine the cross-section of the molecules by measurements of the viscosity, and

thereafter to calculate the coefficients of diffusion and of conductivity for heat of different gases. The agreement between experiment and calculation is in most cases remarkably good, and imparts, therefore, a high degree of probability to these theoretical considerations. This matter is discussed in a very masterly manner in the text-book of O. E. Meyer (second edition, translated by R. E. Baynes, 1899), on the kinetic theory of gases, to which I may therefore refer.

It would seem natural to suppose that the internal friction of a gas would increase with its density. But according to our views the internal friction should be proportional to the number of diffusing molecules in a given volume, *i.e.* to the density, and also to the mean free path of the molecules, which is inversely proportional to the density; hence, according to the kinetic theory of gases, the viscosity of a gas ought to be independent of its density, *i.e.* of its pressure. This conclusion, first arrived at by Maxwell, has also been verified by experimental researches carried out by himself, O. E. Meyer, and other scientists. At very low pressures the law of Maxwell does not hold good, as may be understood from the way in which it was deduced. Another consequence of the theory is, that the viscosity of gases must increase with temperature, because of the increased speed of the molecules. This conclusion, which infers that gases behave in an opposite way to liquids, is also found to be in good agreement with experience.

The viscosity can be easily determined by blowing a current of gas under a definite pressure through a narrow tube. From the viscosity the molecular free path and the total cross-section of the molecules in a given quantity of gas may be determined.

The following table gives some determinations of the viscosity,  $\eta$ , in millionths of absolute units, the molecular free path,  $l$ , in  $10^{-7}$  cm., the total cross-section,  $Q$ , in sq. cm., and the relative volume,  $V$ , of the molecules contained in 1 c.c. gas at  $0^\circ$  C. and 76 cm. pressure. The experiments were carried out by Graham; the table is from O. E. Meyer's book:—

	$\eta$	$l$	Q	$V \times 10^{-6}$
Hydrogen . . . . .	84	17·8	9,900	0·98
Marsh-gas . . . . .	106	8·0	22,200	3·31
Ammonia . . . . .	98	7·1	24,900	3·93
Carbon monoxide . . .	167	9·5	18,700	2·56
Ethylene . . . . .	99	4·2	42,500	8·76
Nitrogen . . . . .	167	9·5	18,600	2·54
Nitric oxide . . . . .	168	9·4	19,200	2·66
Oxygen . . . . .	191	10·2	17,400	2·30
Hydrogen sulphide . . .	118	6·0	29,300	5·01
Hydrogen chloride . . .	141	7·1	25,100	3·98
Carbon dioxide . . . .	145	6·0	27,000	4·44
Nitrous oxide . . . .	144	6·5	27,100	4·46
Methyl ether . . . .	92	4·1	43,500	9·07
Methyl chloride . . . .	105	4·4	40,100	8·03
Cyanogen . . . . .	97	4·0	43,900	9·20
Sulphur dioxide . . . .	125	4·7	37,900	7·36
Ethyl chloride . . . .	95	3·6	49,300	10·95
Chlorine . . . . .	128	4·6	38,800	7·64
Water-vapour ( $15^\circ$ ) . .	97	7·1	24,900	3·93

If we suppose the molecules to be spherical, their relative volumes are proportional to the  $\frac{3}{2}$  power of their surfaces. This is true for the individual molecules, but as 1 c.c. gas at  $0^\circ$  C. and 76 cm. pressure contains the same number of molecules, independently of the nature of the gas, the surface of 1 molecule is proportional to the cross-section of all the molecules. Hence, the figures in the last column of the table, under the heading V, found by raising the numbers given under Q to the power of  $\frac{3}{2}$ , give the relative volume of the molecules, assuming that they are spherical in shape. The cube root of the figures under V gives the relative size of the diameters of the molecules, according to the same hypothesis.

The mean free path does not alter very much; it varies from 3·6 ten-millionths of a centimetre for ethyl chloride to 17·8 for hydrogen. It is still greater for some monatomic gases, namely 24 for helium and 34 for mercury, expressed in the same units.

If we divide the speed of the molecules by the mean free path, we get the number of collisions in one second. This quantity varies from  $4.2 \times 10^9$  for oxygen to  $9.5 \times 10^9$  for hydrogen, among the gases given in the table.

The sum of the cross-sections of all the molecules in 1 c.c. at 0° C. and 76 cm. pressure seems to be very great. It is nearly 1 sq. metre for hydrogen; for most of the other gases which are of simple composition it is about 2 to 3 sq. metres, for chlorine it nearly reaches the value of 4 sq. metres. For the most complex of the gases examined it is nearly 5 sq. metres.

Up to this point the conclusions are fairly trustworthy, but if we wish to proceed further and calculate the real volumes of the molecules and their diameters, we must introduce some new hypothesis. Loschmidt and Lothar Meyer supposed that the real volume of all the molecules in a gas is equal to the volume of this gas after condensation to the liquid state. This hypothesis evidently gives too high a value for the real volume of the molecules, for there must also be some interstices between the molecules in a liquid. Not only do these calculations give too high a value for the volume of the molecules, but also for their diameters.

Another method consists in the observation of the deviations from Boyle's law. Van der Waals has given a physical interpretation of these deviations, and represented it by the formula—

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT.$$

Here  $b$  is four times the real volume of the molecules. From the determination of the relation between the volume and the pressure of a gas  $b$  may be calculated, and with it the real molecular volume.

There is a third method which gives still lower values for the volumes of the molecules, namely, the determination of the dielectric constant or of the refractive index of substances. The real volume  $v$  of the molecules in a gas is connected with the dielectric constant  $K$  by the following formula :—



According to a law deduced by Maxwell,  $K = n^2$ , where  $n$  is the refractive index of the gas in question; hence, it is not necessary to know  $K$  in cases where this law holds good, if  $n$  is determined.

We give a table of the different values of the diameters (in  $10^{-8}$  cm.) calculated according to different methods :—

	From K.	From $n$ .	From $b$ .	From $v$ .
Carbon dioxide . . . . .	1·8	—	6·3	16·2
Hydrogen . . . . .	1·4	—	4·0	30·6
Carbon monoxide . . . . .	1·9	—	—	—
Nitrous oxide . . . . .	1·8	—	—	17·1
Ethylene . . . . .	2·1	—	—	17·0
Marsh-gas . . . . .	2·3	—	—	18·1
Sulphur dioxide . . . . .	6·9	1·7	—	12·1
Ammonia . . . . .	—	1·6	—	—
Water-vapour . . . . .	—	0·9	—	—
Nitrogen . . . . .	—	1·7	—	—
Nitric oxide . . . . .	—	1·6	—	—
Oxygen . . . . .	—	1·6	—	—
Sulphuretted hydrogen . . . . .	—	2·2	—	—
Hydrochloric acid . . . . .	—	1·8	—	—
Cyanogen . . . . .	—	1·9	—	—
Chlorine . . . . .	—	1·9	—	—

Having now found probable values for the diameters of various molecules, it is easy to calculate the number,  $N$ , of molecules in 1 c.c. gas at  $0^\circ$  C. and 76 cm. pressure. We have only to divide the total area  $Q$  of the cross-sections by  $\frac{1}{4}\pi d^2$ , where  $d$  is the diameter of a molecule. This gives the following values for  $N$  :—

	CO <sub>2</sub>	H <sub>2</sub>	CO	N <sub>2</sub> O	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	SO <sub>2</sub>	NH <sub>3</sub>	O <sub>2</sub>	N <sub>2</sub>	
From K	1·1	0·64	0·66	1·06	1·2	0·55	—	—	—	—	$\times 10^{20}$
From $n$	—	—	—	—	—	—	1·7	1·2	0·87	0·84	$\times 10^{20}$
From $b$	0·09	0·08	—	—	—	—	—	—	—	—	$\times 10^{20}$
From $v$	0·013	0·00107	—	0·011	0·019	0·0088	0·038	—	—	—	$\times 10^{20}$

The mean value of  $N$ , calculated from  $K$  and  $n$ , is

$N = 0.98 \times 10^{20}$ , or in round numbers  $100 \times 10^{18}$ ; from  $b$ ,  $8.5 \times 10^{18}$ ; and from  $v$ ,  $1.5 \times 10^{18}$ . Now, according to van der Waals, the real volume is about a fourth of the volume,  $v$ , of the liquid. The last figures are thus about 16 times too small, and on correction would give a value for  $N$  of about  $27 \times 10^{18}$ .

On the other hand, the relation between the dielectric constant ( $K$ ) and the volume of the molecules was developed by Mossotti on the assumption that the molecules are perfect conductors throughout. Now this may be true for the atoms in the molecule, but not for the molecule itself, for because of their rapid rotation around their gravitational centre the atoms collide with foreign molecules which enter within a surface much greater than the cross-section of the atoms, and this surface may be regarded as the cross-section of the molecule. Therefore the values of  $N$  deduced from Mossotti's hypothesis may be regarded as too high. A value of about  $20 \times 10^{18}$  seems to be the most probable.

There is another method of calculating the number of molecules in 1 c.c. of a gas at  $0^\circ\text{C}$ . and 76 cm. pressure. Making use of different theoretical considerations, the electric charge on an atom has been calculated by different investigators. The last determination of its value is due to Planck,<sup>1</sup> who found the atomic charge to be  $4.69 \times 10^{-10}$  electrostatic units. Now, we have seen before that the charge on 1 gram of hydrogen is 96,500 coulombs, or  $28,950 \times 10^{10}$  electrostatic units. Since 1 gram of hydrogen at  $0^\circ\text{C}$ . and 76 cm. pressure occupies 11,200 c.c., the total charge on the atoms in 1 c.c. hydrogen is  $2.59 \times 10^{10}$  electrostatic units. If we divide this value by the value of one atomic charge,  $4.69 \times 10^{-10}$ , we obtain  $55 \times 10^{18}$  as the number of atoms in 1 c.c. hydrogen. This value is double the number of molecules, because one molecule of hydrogen contains two atoms. We are thereby led to the conclusion that the number of molecules in 1 c.c. at  $0^\circ\text{C}$ . and 76 cm. pressure is about  $N = 27.5 \times 10^{18}$ , which agrees fairly well with the value of  $N$  calculated above. (J. J. Thomson<sup>2</sup> gives a value  $N = 36 \times 10^{18}$ , calculated on similar grounds.) The number  $N = 27.5 \times 10^{18}$  gives the cross-section of a hydrogen molecule to be  $360 \times 10^{-18}$

<sup>1</sup> Planck, *Ann. Physik.* (4), 1901, **4**, 566.

<sup>2</sup> J. J. Thomson, *Phil. Mag.* (5), 1898, **46**, 528.

sq. cm., and the diameter to be  $2 \cdot 14 \times 10^{-8}$  cm. This agrees very well with the distance between the hydrogen ions and a metal plate, on which they have been deposited by electrolysis, which distance was previously shown (p. 93) to be approximately equal to the radius of the hydrogen molecule, namely,  $1 \times 10^{-8}$  cm. The distance between the centres of two molecules in a gas at 0° C. and 76 cm. pressure is about 30 times greater ; it is—

$$\sqrt[3]{\frac{1}{N}} = \frac{1}{3} \times 10^{-6} \text{ cm.}$$

There are many other methods of calculating the number N, and as a mean value  $N = 21 \times 10^{18}$  is generally accepted.

A better agreement must not be expected. We have supposed that the space surrounding a molecule, and into which no foreign matter can penetrate, is spherical in shape. This is probably only a rough approximation. O. E. Meyer has endeavoured to show that the molecules have a flat shape, but his proof does not seem to be very strict, as pointed out by Ostwald.<sup>1</sup>

The kinetic theory of gases was for a long time held in the highest estimation. Boyle's law may be derived from it very simply, and many laws and regularities regarding specific heat, viscosity, conductivity for heat, diffusion, and also, recently, laws regarding the breadth of the lines of the spectrum (Michelson),<sup>2</sup> were discovered with the help of this theory. But, on the other hand, the law of Avogadro can only be deduced with great difficulty, and many of the newer developments of this theory are characterized by their lack of simplicity. We must therefore say that this theory is in many cases an instrument which is very difficult to manipulate, and the value of theories, as of instruments, depends on their easy applicability. This circumstance has led to a depreciation of this theory in later times, which is no more justified than the over-estimation of it some thirty years ago.

The kinetic theory of gases gives a simple explanation of

<sup>1</sup> Ostwald, "Lehrbuch d. allg. Chemie," 2nd edit., vol. i. p. 215. Leipzig : 1891.

<sup>2</sup> Michelson, *Phil. Mag.* (5), 1892, 34, 280.

certain facts, which are of great interest, respecting the atmospheres of celestial bodies. Johnstone Stoney called attention to the fact that a body moving upwards with the velocity of 11·2 km. per second could not be retained in the neighbourhood of our planet under the influence of its gravitational attraction, but would fly away into infinite space (if it were not held back by the sun's attraction). For the moon and the sun the corresponding critical velocities are 2 km. and 613 km. per second respectively. Now, we have seen previously that hydrogen molecules at 0° C. move with a mean velocity of 1·828 km. per second. The highest temperature on the moon's surface (the centre of the full moon) is about 150° C., and consequently the velocity of hydrogen molecules at that place would be about 2·33 km. per second, *i.e.* above the critical speed. Therefore, hydrogen must disappear from this point of the moon, and since new hydrogen diffuses to it as long as there is any remaining, the hydrogen, if it once existed on the moon, would have very soon disappeared from it.

The same reasoning holds good for oxygen. The velocity of its molecules is about one-fourth of that of the hydrogen molecules, *i.e.* about 0·58 km. per second at 150° C. This is only 0·29 of the critical speed. But according to Maxwell's law of distribution, about 0·03 % of all the oxygen molecules have a higher speed than the critical one, and in course of time the oxygen also would have disappeared from the moon's surface. The same is valid for the nitrogen, and in a slightly less degree for the argon, and therefore it is no wonder that we find no trace of an atmosphere on the moon. Carbon dioxide, which may originally have existed on the moon, will in course of time have been absorbed through the process of weathering.

We may now apply the same reasoning to the earth's atmosphere. We know, however, that the temperature is much lower in the upper layers of the atmosphere than at the earth's surface, and this objection has been made to Stoney's ideas. Stoney<sup>1</sup> points to the fact that helium is supplied from springs in about 3000 times as great a quantity as if it were absorbed

<sup>1</sup> Stoney, *Astrophysical Journ.*, 1898, 7, 25; 1899, 9, 1; 1900, 11, 251 and 357. *Nature*, 1899, 61, 515.

from the air. Therefore, if the helium did not flow away from the atmosphere as rapidly as it is produced, we might expect a much higher quantity of this gas in the air than that now observed (about a millionth of the total volume). And, further, if absolutely no helium escaped from the earth, the air should contain about 3000 times more helium than it does.

The molecular speed of helium at 0° C. is 1·12 km. per second, about the tenth part of the critical speed for the earth's atmosphere. Observations of the temperature of the upper layer of the earth's atmosphere seem to indicate that from a certain height onwards the temperature sinks very slowly. Probably in the highest layers the temperature rises again, and, in the neighbourhood of solid particles of cosmical dust, it may even rise to between 50° and 60° C. on the side towards the sun. Even at that temperature the helium molecules would escape so slowly from our atmosphere (less than 1 c.mm.—at 0° and 760 mm.—in one year) that they may practically be regarded as bound to the earth's atmosphere.

According to the calculation of Cook, at 5° C.  $10^{-10}$  c.c. of helium (at atmospheric pressure) would escape in one year. Therefore Cook<sup>1</sup> concluded that the helium must have already disappeared at the time when the earth was a gaseous ball of much less density and higher temperature than now (as, e.g., in the case of Jupiter). This conclusion must be supported by a research showing that the total supply of helium from springs during the period which has since elapsed has not been greater than the present quantity of helium in the air.

Stoney's hypothesis must, as will be seen from these considerations, be worked out much more fully than it is at present.<sup>2</sup> But it gives a tempting explanation of the fact that the density of the atmospheres of celestial bodies generally increases with their mass. For instance, Mercury seems to resemble the moon and the planetoids in lacking an atmosphere; Mars has a very rare atmosphere; Venus, about the same as that of the earth; and the large outer planets possess very dense atmospheres. Their low densities seem even to

<sup>1</sup> Cook, *Nature*, 1904, **69**, 487.

<sup>2</sup> Cf. v. Smoluchowski, *Physik. Zeit.*, 1901, **2**, 307; Rogovsky, *Astrophys. Journ.*, 1901, **14**, 234.

indicate that they consist entirely of gaseous masses surrounded by clouds.

In the celestial nebulae, where the gravitational forces—in consequence of the tenuity of matter—are very small, the loss of gases by reason of their molecular movement probably plays a most important *rôle*. During this process the so-called entropy decreases, whereas it increases on the denser celestial bodies such as the sun (and other stars) and the planets. Because of this it is possible that the entropy decreases just as much in one part of the universe—the nebulae—as it increases in another part—the stars and planets—so that, on the average, it remains constant. It is only in this manner that one can conceive why the processes going on in the universe have not already come to an end.

## CHAPTER X

### *CHEMICAL KINETICS AND STATICS*

EARLY in the history of science it had been found that different acids have a very different affinity for the same base, and in this sense it was said that sulphuric acid is the strongest of all acids, for by means of it it is possible to drive out all other acids from their salts. Chemists, therefore, in the eighteenth century had their chief attention directed to the construction of so-called "tables of affinity," in which the substances (*e.g.* different metals, hydrogen, carbon, etc.) were arranged according to their ability to replace each other in compounds (*e.g.* in oxides). The latter part of Berzelius' series is such a table, in which the metals are arranged according to their ability to replace each other from solutions of their salts.

The opinions of the chemists of the eighteenth century were collated by the Swedish chemist Bergman, who collected the experimental knowledge of his time in a great number of tables, from which he drew general conclusions. He introduced the two new conceptions of chemical substitution, *i.e.* the replacement of one substance by another, and of double decomposition, *i.e.* the mutual exchange of constituents between two compounds.

Generally speaking, it may be said that the theoretical ideas of Bergman prevailed till lately. The principal doctrine in Bergman's system is that chemical processes are complete, and never limited. This opinion is also the fundamental one of the thermochemical systems, of which the most elaborate is that of Berthelot. According to Thomsen and Berthelot, of a number of possible chemical reactions, that one always takes place which is accompanied by the greatest evolution of heat.

It is very remarkable to note that, although Bergman (1783) supposed that chemical forces are of the same nature as gravitational forces, he nevertheless was able to build up his chemical system. Of course he was not sufficiently acquainted with physics to understand the untenability of his position. This the French physical chemist Berthollet pointed out. We find in his work (1803)<sup>1</sup> the idea expressed that if several acids act simultaneously on an insufficient amount of a base, they each combine with a part of it, the amount depending on their affinities and their relative masses. It is much to be deplored that he regarded the equivalent weights as a measure of the inverse value of the affinities, instead of trying to determine them experimentally. In reality, he put forward the wholly false hypothesis that all acids are of the same strength, if they are present in equivalent proportions. Berthollet regarded all reactions as incomplete, and introduced the idea of "chemical equilibrium." For the equilibrium in a solution, it is of the highest importance to take into account whether any of the substances easily separate from the solution in the gaseous or solid form. The portions which separate out have no influence upon the equilibrium.

The chemists who followed Berthollet were not sufficiently trained in theoretical work to understand and further develop his brilliant ideas. His contemporary Gay-Lussac, however, worked on the same lines as Berthollet; he supposed that if two or more salts are dissolved together in water, then all the possible salts, that could be formed from the original salts by double decomposition, exist in the solution.

Rose also did not allow himself to be guided by the ideas of his time, but upheld the notion of a mass-action. He found that a solution of a sulphide contains free sulphuretted hydrogen, which could be driven off by boiling. He also showed that the quantity of free sulphuretted hydrogen increased with the quantity of water used as solvent. This case is thus a typical example of chemical mass-action.

According to him, the weathering of rocks furnishes us with another example of this action; *e.g.* felspar is decomposed

<sup>1</sup> Berthollet, "Untersuchungen über die Gesetze der Verwandschaft;" Ostwald's *Klassiker*, No. 74.

by the long-continued action of such weak acids as carbonic acid and water, whereas in ordinary laboratory work it cannot be decomposed excepting by the strongest chemical agents. It is the great mass of carbonic acid and water, supplied from the air during a considerable time, that produces this wonderful, and for agriculture so important, action. Further, Rose showed that the decomposition of salts of antimony, bismuth, and mercury depends upon the water acting as a base, and competing with the weak bases of these salts according to their relative masses.

It had already been observed by Marggraf in the eighteenth century that "sulphate of baryta" may be partially transformed into "carbonate of baryta" and alkali-sulphate by the addition of alkali-carbonates. This reaction could also, as was well-known, be carried out in the opposite direction, so that on the addition of alkali-sulphate to barium carbonate, barium sulphate and alkali-carbonate were formed. This case of mass-action was studied more closely by Dulong and Rose, but Malaguti first gave the complete explanation of it. He also studied other similar cases, for instance,  $\text{BaHPO}_4$  and  $\text{K}_2\text{CO}_3$ ,  $\text{BaCO}_3$  and  $\text{Na}_2\text{CrO}_4$ . He tried to show that the equilibrium was independent of the way in which the salts were mixed; for instance, the end result was the same, if he started with  $\text{BaCO}_3$  and  $\text{K}_2\text{SO}_4$  (and a given quantity of water), or with  $\text{BaSO}_4$  and  $\text{K}_2\text{CO}_3$ , if he only used equivalent quantities. Malaguti also dissolved two salts in water, *e.g.* potassium acetate and lead nitrate, and precipitated them by adding alcohol. He found that the precipitate showed the conversion of this system into that of potassium nitrate and lead acetate to the extent of 92 %. On dissolving the two latter salts and precipitating, he found that 9 % had been converted. Evidently he should have found 8 %, and then the final result would have been independent of the starting-point.

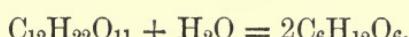
In 1853, Malaguti expressed the fundamental idea, that the equilibrium is due to the circumstance that two opposite processes are going on with the same velocity. For instance, if we bring together  $\text{BaSO}_4$  and a solution of  $\text{K}_2\text{CO}_3$ ,  $\text{K}_2\text{SO}_4$  and  $\text{BaCO}_3$  are formed at first with a certain velocity, but from the molecules  $\text{K}_2\text{SO}_4$  and  $\text{BaCO}_3$  the original system,  $\text{K}_2\text{CO}_3$  and

$\text{BaSO}_4$ , is reproduced. The velocity with which this regeneration takes place increases with the quantity of  $\text{K}_2\text{SO}_4$  formed, and the velocity of the formation of  $\text{K}_2\text{SO}_4 + \text{BaCO}_3$  decreases at the same time, owing to the diminution in the quantity of the original salts. Therefore, when a certain concentration of  $\text{K}_2\text{SO}_4$  is reached, both the processes go on at the same rate, so that no further change occurs. It is an "equilibrium mobile." To represent it van't Hoff uses the sign  $\rightleftharpoons$ ; e.g.—



These reactions in heterogeneous systems are much more difficult to study than those in homogeneous systems, for their velocity, *i.e.* the quantity transformed in unit of time, depends on convection currents in the liquid, and on the state of the solid body (as, for example, the size of its particles, how much it has been heated before the reaction, and so on); moreover, these reactions generally go on very slowly. Already, in 1777, Wenzel had drawn attention to the velocity of reaction when a metal is dissolved by an acid. He put forward the hypothesis, without experimental verification, that the velocity of the reaction is proportional to the concentration of the acid. Berthollet had similar theoretical views: according to him, a reaction would proceed with a velocity proportional to the quantity of reacting substances which remained to be transformed in order to attain equilibrium.

A short time before the researches of Malaguti, Wilhelmy<sup>1</sup> had measured with great exactitude the velocity of transformation during a catalytic process, namely the transformation (inversion) of cane-sugar and water into dextrose and lævulose, according to the equation—



Cane-sugar is dextrorotatory towards polarized light, whereas the mixture of dextrose and lævulose is lævorotatory. This change of the angle of rotation had been long used for determining, by means of instruments called saccharimeters, the quantity of cane-sugar in a solution. Wilhelmy studied the progress of the reaction with time by the help of such an instrument (1850). The process may be carried on at high

<sup>1</sup> Cf. Wilhelmy, "Über das Gesetz," etc.; Ostwald's *Klassiker*, No. 29.

temperatures (above 100° C.) by heating the sugar solution in autoclaves, but also at lower temperatures by adding an acid. Such processes as will only proceed to any appreciable extent (at all events, at lower temperatures) after the addition of a chemical reagent, which is not used up in the reaction, are called catalytic (after Berzelius). The catalytic agent in this case is the acid.

Wilhelmy supposed that the quantity inverted in unit of time at constant temperature is proportional to the quantity of cane-sugar present in the solution. If the time is expressed by  $t$  and the inverted quantity by  $x$ , the velocity of inversion is  $\frac{dx}{dt}$ . This is, according to Wilhelmy, proportional to the quantity of cane-sugar remaining, which may be represented by  $(A - x)$ , if  $A$  is the quantity of cane-sugar at the beginning. This gives the equation—

$$-\frac{dx}{dt} = K(A - x)$$

where  $K$  is called the velocity constant of the reaction. This, on integration, gives—

$$\log A - \log (A - x) = K_1 t$$

where  $K_1 = \frac{1}{2.3025} K$ , using common logarithms. Wilhelmy found that this equation was verified by his experiments, as the following example, using nitric acid at 15° C., shows :—

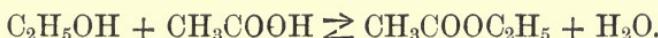
$t$ (in minutes).	$A - x$ .	$\log \frac{A}{A - x}$	$K_1 = \frac{1}{t} \log \frac{A}{A - x}$
0	65.45	—	—
45	56.95	0.0605	0.00134
90	49.45	0.1217	0.00135
150	40.70	0.1981	0.00132
210	33.70	0.2880	0.00137
270	26.95	0.3851	0.00142

$(A - x)$  was put proportional to the observed angle of rotation

at the time of observation, diminished by the angle of rotation at the end of the reaction. Wilhelmy also found that temperature has a great influence on the velocity of reaction. He studied the catalytic effects of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and  $\text{H}_3\text{PO}_4$ .

Many similar experiments have been carried out on a large number of reactions, and the law found by Wilhelmy has been completely verified, especially by Ostwald, who also investigated the hydrolysis of methyl acetate by different acids. Many other catalytic reactions have been studied since, especially by Ostwald and van't Hoff.

In 1862–1863 Berthelot and Péan de St. Gilles investigated the formation of esters from organic acids and alcohols. Here a very interesting case of chemical equilibrium occurs. For instance, if we use equivalent quantities of ethyl alcohol and acetic acid, they are converted into ethyl acetate and water to the extent of two-thirds; and, inversely, if equivalent quantities of ethyl acetate and water are allowed to interact long enough, they are converted into alcohol and acid to the extent of one-third, according to the equation—



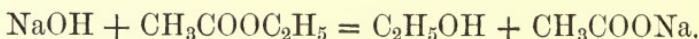
The quantity of acid present was determined by titration, and in this manner the progress of the reaction could be followed. The limiting value to which the process tends is approximately the same for different acids and alcohols; it was found, in thirty different combinations, not to vary more than between 61·3 and 72 % of the quantities of alcohol and acid used. The velocity of the reaction was found to be dependent on the concentrations of the reacting substances, and the authors came to the correct conclusion, that (at the beginning of the process) it is proportional to the product of both the concentrations. Benzene and acetone were used as diluents. Reactions in the gaseous state were also examined.

The influence of temperature on the velocity of reaction is very pronounced; thus the velocity is about 500 times greater at  $100^\circ$  than at  $8^\circ$  C. On the other hand, pressures from 1 to 80 atmospheres have very little influence<sup>1</sup> on reactions

<sup>1</sup> Cf. Rothmund, *Zeit. physikal. Chem.*, 1896, **20**, 168.

in liquids. By using greater proportions of alcohol to one equivalent of acetic acid, the quantity of this substance transformed increases, and if the quantity of alcohol, expressed in equivalents, is 50 times that of the acid, the latter is practically completely transformed when equilibrium is reached.

Another reaction, in which two substances interact so that both substances are transformed, is the saponification of ethyl acetate by means of a base, such as sodium hydrate. This reaction is practically complete, so that the whole quantity either of the ester or of the sodium hydrate is transformed according to the equation—



This reaction is easily followed by titration, at definite intervals of time, of the base still remaining. It was first studied by Warder,<sup>1</sup> in 1881. Weak solutions (0·05 normal or less) had to be used in order to give a reaction sufficiently slow to enable measurements to be made. The velocity of reaction,  $-\frac{dx}{dt}$ , is proportional to the concentration of the base,  $(A - x)$ , and of the ester, also  $(A - x)$ , if the reacting substances are used in equivalent quantities).

The reaction-velocity is therefore—

$$-\frac{dx}{dt} = K(A - x)^2$$

where  $K$  is the velocity-constant; this on integration gives—

$$\frac{1}{A - x} - \frac{1}{A} = Kt; \text{ or } \frac{x}{A(A - x)} = Kt.$$

Warder found the following values,  $A$  being 16 :—

$t$ (min.)	$x$	$\frac{x}{(A - x)}$	$\frac{x}{t(A - x)} = KA$
5	5·76	0·563	0·113
15	9·87	1·601	0·107
25	11·68	2·705	0·108
35	12·59	3·69	0·106
55	13·69	5·94	0·108
120	14·90	13·55	0·113

<sup>1</sup> Warder, *Ber.*, 1881, **14**, 1361.

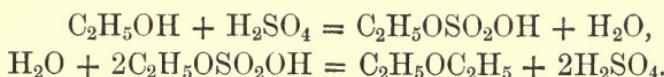
Researches on this reaction have since been carried out on a large scale by Spohr,<sup>1</sup> myself,<sup>2</sup> and others. They all confirm the conclusions of Warder.

This reaction is an example of the so-called bimolecular reactions, where two molecules interact. Properly speaking, the inversion of sugar is also a bimolecular reaction, because, in addition to the cane-sugar, water is used up; but the water is present in such great excess that its quantity does not sensibly alter during the process. Therefore it may be put as a constant in the equation, which in this way becomes similar to that for so-called monomolecular reactions.

A great number of bimolecular reactions have been studied by Hood<sup>3</sup> (1878), Ostwald<sup>4</sup> (1884), Schwab<sup>5</sup> (1884), van't Hoff<sup>5</sup> (1884), and others.

The presence of neutral salts exerts a small influence upon the velocities of reaction; in most cases they accelerate, but sometimes they retard, the reaction. An explanation of this effect is still wanting.

In 1851, Williamson studied the reaction between ethyl alcohol and sulphuric acid, by which ethyl ether is formed. The sulphuric acid is not used up during the process, which is therefore catalytic. To explain the formation of the ethyl ether, Williamson supposed that at first an intermediate product was formed, namely, ethyl sulphuric acid, which then regenerated sulphuric acid according to the following equations:—



This process is therefore characterized by a continual change of place of the reacting atomic groups. In the same manner he supposed that in a quantity of hydrochloric acid, HCl, a hydrogen atom does not remain combined with the same chlorine atom the whole time, but that a continuous interchange takes place.

<sup>1</sup> Spohr, *Zeit. physikal. Chem.*, 1888, **2**, 194.

<sup>2</sup> Arrhenius, *Zeit. physikal. Chem.*, 1887, **1**, 110; 1888, **2**, 284.

<sup>3</sup> Hood, *Phil. Mag.* (5), 1878, **6**, 371.

<sup>4</sup> Ostwald, *J. pr. Chem.*, 1884, **27**, 1.

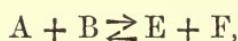
<sup>5</sup> Cf. van't Hoff, "Studien zur chem. Dynamik. bearb. von Cohen," pp. 4-26 (1896).

The explanation by means of intermediate products which Williamson gave for the formation of ethyl ether is generally accepted for the explanation of catalytic processes. In 1857, Clausius worked out an hypothesis, similar to that of Williamson on the exchange of atoms between molecules, in that he assumed a continuous exchange of ions between the molecules of an electrolyte, in order to explain the conduction of the electric current. He pointed out that at one and the same time probably only very few molecules exchange their ions for the ions of other molecules.

Theoretical work of the greatest importance was carried out by the Norwegian scientists Guldberg and Waage,<sup>1</sup> who attempted to deduce theoretically all the laws of velocity of reaction and of chemical equilibrium (1864, 1867, 1879). Their method of looking at things was very similar to that of Berthollet, but they formulated everything much more clearly. If two substances, A and B, interact, the velocity of reaction at constant temperature is—

$$v = k \cdot C_A \cdot C_B,$$

where  $C_A$  and  $C_B$  represent the concentrations of the two substances, and  $k$  is a constant which increases with the temperature. If by the interaction of A and B the substances E and F are formed according to the chemical equation—



an equilibrium is reached after a certain time. This is characterized by the opposite reactions having equal velocities, so that—

$$kC_A C_B = k_1 C_E C_F.$$

This is valid for homogeneous equilibria. If a solid substance separates out during the reaction—if, for instance, E is a precipitate—then Guldberg and Waage found that its “active mass”  $C_E$  behaved as if it were a constant. This is easily understood, for the reacting quantity of this substance is the dissolved part of it, and therefore its concentration  $C_E$  is equal to

<sup>1</sup> Guldberg and Waage, “Untersuchungen über d. chem. Affinität.” Ostwald’s *Klassiker*, No. 104.”

its (constant) solubility. If two of the substances are solid bodies, as in the equilibrium—



the concentrations of both of them must be constant; if the solubilities of the two substances are  $B$  and  $F$ , we get—

$$kC_B = k_1 C_E F$$

or—

$$\frac{C_A}{C_E} = \text{const.}$$

In the dissolution of a solid substance its "active mass" should be put proportional to the surface attacked.

Guldberg and Waage have themselves verified their conclusions by studying the velocity of solution of a metal in different acids. They have also studied the reaction between potassium or sodium carbonate and barium sulphate. Suppose at the beginning  $p$  equivalents of potassium sulphate and  $q$  equivalents of potassium carbonate were dissolved in one litre, and the solution shaken with a mixture of powdered barium sulphate and barium carbonate; if  $x$  equivalents of the potassium sulphate were converted into carbonate, we might expect that—

$$\frac{p - x}{q + x} = \text{const.}$$

Analysis of the solution gave the following figures:—

$p$	$q$	$x$	$\frac{p - x}{q + x}$
200	0	39.5	4.06
250	0	50.0	4.00
350	0	71.9	3.87
250	25	30.0	4.00
300	25	40.8	3.94
200	50	0.5	3.95   Mean 3.97

As can be seen from these figures, the proportion of potassium carbonate ( $p - x$ ) to potassium sulphate ( $q + x$ ) at the end of the reaction is constant, as the theory demands. The equilibrium was also found to be independent of the relative quantities of

sulphate and carbonate of barium added at the beginning of the experiment.

In 1868, the Danish thermochemist Jul. Thomsen carried out an investigation on the equilibrium existing in a homogeneous system. He made use of thermochemical measurements.<sup>1</sup> If we neutralize sulphuric acid with caustic soda, both in very dilute solution (1 gram equivalent dissolved in 1800 grams water), the heat evolved is 15,700 cal. per gram equivalent. If we in the same way neutralize one gram equivalent of monochloracetic acid, the heat of neutralization is 14,300 cal. If we now add 1 gram equivalent of sulphuric acid (49 grams) to a solution of 1 gram equivalent of monochloracetate of sodium (117·5 grams), the evolution of heat should be  $15,700 - 14,300 = 1400$  cal., if the sulphuric acid completely replaces the monochloracetic acid. If no reaction takes place, no heat will be evolved. In reality, we find an intermediate value between these two extremes, namely, 1183 cal. ( $= 0.845 \times 1400$ ). This indicates that the sulphuric acid is neutralized to the extent of 84·5 %, and that 15·5 % of the sodium monochloracetate remains intact. There exists, therefore, a chemical equilibrium between sulphuric acid (15·5 %), sodium sulphate (84·5 %), monochloracetic acid (84·5 %), and sodium monochloracetate (15·5 %). Thomsen then asserted that the strength or "avidity" of the sulphuric acid is  $\frac{84.5}{15.5} = 5.44$  times greater than that of the monochloracetic acid.

Instead of the heat of neutralization, it is possible to use any other property which alters on neutralizing acids with bases, for the investigation of the relative avidities of acids and of the corresponding property of bases. Ostwald<sup>2</sup> made use of the change of volume occurring on neutralization, which may be measured simply by determining the specific gravities of solutions of one gram-molecule of acid, base, and salt in 1, 1, and 2 litres of water respectively. Another property used by Ostwald<sup>3</sup> was the molecular refraction of the same solutions.

<sup>1</sup> Thomsen, *Ann. Physik u. Chem.* (2), 1869, 138, 65.

<sup>2</sup> Ostwald, *J. pr. Chem.* (2), 1877, 16, 385.

<sup>3</sup> *Ibid.*, 1878, 18, 328.

By means of these different methods a great number of data regarding the relative avidities of acids and bases have been collected.

The discussion of these data will find its proper place later on in the consideration of the theory of electrolytic dissociation. It may suffice now to state that, according to these determinations, the chemical equilibria which exist in these cases are in accordance with the theory of Guldberg and Waage.

The classical example of equilibrium in a homogeneous solution is that studied by Berthelot and Péan de St. Gilles and referred to previously. They found, as pointed out before, that on adding one gram-molecule of acetic acid to one gram-molecule of ethyl alcohol, equilibrium is reached as soon as these are transformed to the extent of two-thirds into ester and water. This corresponds to the equilibrium equation—

$$4(p - x)(1 - x) = x^2,$$

where  $p$  is the number of gram-molecules of alcohol added, the quantity of acetic acid added being one gram-molecule, and  $x$  is the number of gram-molecules transformed. If  $p = 1$ , equilibrium is reached when  $x = \frac{2}{3}$  and  $p - x = 1 - x = \frac{1}{3}$ , by which value the equation evidently is satisfied.

In 1877, using this equation, van't Hoff<sup>1</sup> calculated  $x$  for different values of  $p$ , and compared his results with the results of the measurements made by Berthelot and Péan de St. Gilles. He thus found the following calculated values, tabulated at the side of the observed values, corresponding to different quantities of  $p$  :—

$p$	$x_{\text{obs.}}$	$x_{\text{calc.}}$	$p$	$x_{\text{obs.}}$	$p_{\text{calc.}}$
0·05	0·05	0·049	1·5	0·792	0·785
0·18	0·171	0·171	2	0·855	0·845
0·28	0·226	0·232	3	0·89	0·902
0·33	0·293	0·311	4	0·90	0·93
0·50	0·422	0·423	8	0·97	0·95
0·67	0·533	0·528	12	0·93	0·98
1·0	0·670	0·667	19	0·95	0·99

If we except the last figures, the agreement between the

<sup>1</sup> Van't Hoff, *Ber.*, 1877, 10, 669.

observed and calculated values is very good, and generally we may regard these data as a good confirmation of the law of Guldberg and Waage.

Very soon after the work of Guldberg and Waage (1869) came the theoretical research of Horstmann,<sup>1</sup> who deduced the laws of equilibrium for gases, by means of thermodynamical considerations. His results agree with those of Guldberg and Waage. The same holds for his results regarding the heterogeneous equilibria with one gaseous phase. In the years 1876–1878, the memorable theoretical investigations of Willard Gibbs<sup>2</sup> appeared, which, however, remained for a long time without influence.

In 1877, Ostwald began his wide-reaching researches on these subjects. He studied the velocities of different reactions, such as the inversion of cane-sugar, the saponification of methyl acetate, and the conversion of acetamide and water by an acid into acetic acid and the ammoniacal salt of this acid.<sup>3</sup> He determined the "avidities" of the acids in homogeneous equilibria, as has been already mentioned, and in connection with heterogeneous equilibria he studied the solution of sulphide of zinc and of calcium oxalate.<sup>4</sup> In these researches he used a very great number of acids (thirty-three) at different concentrations. He found that the order of the acids is always the same, the most active being hydrochloric, hydrobromic, nitric, chloric, and certain sulphur acids. In the inversion of cane-sugar and the saponification of methyl acetate he found that the different acids have (nearly) the same relative strengths. If we take the strength of hydrochloric acid as unit, that of citric acid is 0·017, as determined by means of the inversion of cane-sugar, and 0·016 from measurements on the catalysis of methyl acetate.

In the determination of the relative strength of acids by means of the acetamide reaction, and by means of the solution of

<sup>1</sup> Horstmann, *Ber.*, 1869, **2**, 137; 1871, **4**, 635; *Ann. d. Chem. u. Pharm.*, Suppl., 1870, **8**, 112; 1893, **170**, 192.

<sup>2</sup> Gibbs, *Trans. of the Connecticut Acad.*, 3, 1876–1878.

<sup>3</sup> Ostwald, *J. pr. Chem.* (2), 1883, **27**, 1; **28**, 449; 1884, **29**, 385.

<sup>4</sup> *Ibid.*, 1878, **18**, 342; 1879, **19**, 468; 1880, **22**, 251, and **23**, 517; 1883, **28**, 494.

difficultly soluble salts, the circumstances are not so simple as in the above cases. This is due to the formation of neutral salts during the reactions, whereby the simple laws are obscured. Later on, after the introduction of the theory of electrolytic dissociation, these disturbing circumstances were easily understood, as we shall see later.

## CHAPTER XI

### THE INFLUENCE OF TEMPERATURE AND PRESSURE. DISSOCIATION

In the study of the so-called "abnormal" vapour densities we have already found that some molecules, for instance those of ammonium chloride, are split up into two (or more) simpler molecules on raising the temperature. This process is called dissociation. The laws of dissociation were first studied by St. Claire Deville. Dissociation is a so-called reversible process, *i.e.* on lowering the temperature the products of dissociation re-combine. A chemical equilibrium exists between the original molecules and the products of their decomposition, and the study of the laws of this equilibrium may be effected by the help of thermodynamics. This study has been very fruitful for theoretical chemistry, and we will, therefore, consider the phenomenon of dissociation a little more in detail.

The simplest case of dissociation is that presented by the molecules of iodine, which at low temperatures are composed of two iodine atoms and at higher temperatures are split up into simple atoms, as the molecular weight determinations by Victor Meyer<sup>1</sup> and Crafts,<sup>2</sup> have made evident. They found the following vapour densities at the pressures 0·1, 0·2, 0·3, and 0·4 atmospheres and at the given temperatures, referred to air at the same pressure and temperature:—

Temp.	$p = 0\cdot 1$	$p = 0\cdot 2$	$p = 0\cdot 3$	$p = 0\cdot 4$
650°	8·8	8·8	8·8	8·8
800°	7·42	7·88	8·21	8·52
900	6·58	7·22	7·45	7·78
1000	5·95	6·72	6·83	7·15

<sup>1</sup> Meyer, *Ber.*, 1880, **13**, 394.

<sup>2</sup> Crafts, *Compt. rend.*, 1880, **90**, 184.

Temp.	$p = 0\cdot 1$	$p = 0\cdot 2$	$p = 0\cdot 3$	$p = 0\cdot 4$
1100	5·40	6·00	6·24	6·44
1200	4·92	5·36	5·62	5·82
1300	4·6	4·82	5·02	5·25
1400	4·5	4·54	4·73	5·0
1500	4·48	4·52	4·61	—

The density 8·8 corresponds to the molecular weight  $I_2 = 254$ , the density 4·4 to the total dissociation into atoms,  $I = 127$ . At temperatures from  $350^\circ$  to  $650^\circ$  no appreciable dissociation takes place; at  $800^\circ$  already about 30 % of the molecules are dissociated at the lowest pressure, but only 21, 14, and 7 % respectively at the higher pressures. At higher temperatures the dissociation increases very rapidly; up to about  $1200^\circ$  the increase in the "degree of dissociation," *i.e.* in the fraction of dissociated molecules, is about 15 % for an increase in temperature of  $100^\circ$ . At higher temperatures there are not many molecules remaining to be dissociated, therefore the degree of dissociation now increases slowly with temperature, and at about  $1600^\circ$  C. the dissociation may be regarded as practically complete.

Already in 1869 Horstmann<sup>1</sup> had deduced by means of thermodynamics that for the equilibrium expressed by the equation—



the following relation must hold good :—

$$(Conc. of I_2-molecules) = \text{const} \times (\text{conc. of I-molecules})^2.$$

This relation may be deduced from Guldberg and Waage's law, and also from kinetic considerations, in the following very simple manner. The number of  $I_2$ -molecules which are decomposed in a second is proportional to the concentration of these molecules, and the number of  $I_2$ -molecules re-formed from two  $I$ -molecules is proportional to the number of collisions per second between the latter, and this number is, as may easily be seen, proportional to the square of their concentration. When equilibrium is reached, no increase or decrease in the number of  $I_2$ -molecules occurs; and therefore the number of  $I_2$ -molecules decomposed in unit of time must be equal to the

<sup>1</sup> Horstmann, *Ber.*, 1869, 2, 137.

number of  $I_2$ -molecules regenerated in the same time, and we are thus led to the above equation.

From this equation it follows that the degree of dissociation increases as the pressure is diminished. For if the pressure is decreased so much that the concentration of the  $I$ -molecules sinks to half its former value, the concentration of the  $I_2$ -molecules must simultaneously decrease to the fourth of the original value. In other words, the relative number of the  $I$ -molecules, or the degree of dissociation, is increased on expansion (if the temperature remains constant). We also see from the above table that the lower the pressure the less is the vapour density.

This is a special case of a general law. If there is equilibrium between two systems of molecules (here  $I_2$  and  $2I$ ), of which the one (here  $2I$ ) occupies the greater volume at the given pressure, then a decrease in pressure brings about an alteration in favour of this system ( $2I$ ). By means of thermodynamics, Planck has deduced the following equation for this process—

$$RT \frac{d \log_e \text{const.}}{dp} = \Delta.$$

where  $T$  is the absolute temperature,  $R$  is 82.9 atmospheres per square centimetre,  $p$  the pressure in atmospheres,  $\Delta$  the alteration in volume (in cubic centimetres) at constant pressure, the reaction taking place between the number of gram-molecules indicated by the chemical equation, and "const." is the constant in the equation of equilibrium.

There is an analogous law for the alteration of the equilibrium with temperature; namely, if equilibrium exists between two systems of molecules (here  $I_2$  and  $2I$ ), of which the one (here  $2I$ ) is formed from the other by absorption of heat, then a rise in temperature alters the equilibrium in favour of this system.

From thermodynamical considerations we may deduce the following equation (of van't Hoff):—

$$\frac{d \log_e \text{const.}}{dt} = - \frac{W}{1.99T^2}$$

where  $W$  represents the so-called heat of dissociation (at constant pressure), that is, in the present case, the heat absorbed during the transformation of 1 gram-molecule (= 254 grams)

$I_2$  into 2 gram-molecules I; T is the absolute temperature, and  $\frac{d \log_e \text{const.}}{dt}$  is the increase in the natural logarithm of the constant in the above formula, divided by the corresponding increase in the temperature. With the aid of this formula Boltzmann<sup>1</sup> calculated the heat of dissociation of 1 gram-molecule  $I_2$  to be 28,500 cal.

Bromine behaves in nearly the same manner as iodine, according to experiments of V. Meyer and Langer,<sup>2</sup> except that the dissociation is less at the same temperatures. At 900° the degree of dissociation is inappreciable; at 1200° it reaches 40%, and at a white heat (about 1450° C.) 75% (all at atmospheric pressure).

Another example is the dissociation with increasing temperature of  $N_2O_4$  into 2NO<sub>2</sub>. It has been studied by many physicists, among others by St. Claire-Deville and Troost,<sup>3</sup> A. Naumann,<sup>4</sup> W. Gibbs, Horstmann, E. and L. Natanson.<sup>5</sup> The following data, which are valid for atmospheric pressure, are given by St. Claire-Deville and Troost:—

Temp.	26·7	39·8	49·6	60·2	70·0	80·6	90·0	100·1	111·3	121·5	135·0
Density	2·65	2·46	2·27	2·08	1·92	1·80	1·72	1·68	1·65	1·62	1·60
Percentage dissociation}	20·0 29·2 40·0 52·8 65·6 76·6 84·8 89·2 92·1 96·2 98·7										

The density of  $N_2O_4$  is 3·18, that of NO<sub>2</sub>=1·59. In this case the dissociation is considerable, even at comparatively low temperatures.

Another system, the dissociation of hydriodic acid (2HI) into hydrogen (H<sub>2</sub>) and iodine (I<sub>2</sub>), has been studied by Hautefeuille and Lemoine. In this case the number of molecules is not altered during the transformation, and therefore the pressure has no influence upon the equilibrium, as Lemoine<sup>6</sup> proved.

<sup>1</sup> Boltzmann, *Ann. Physik. u. Chem.*, 1884, **22**, 68.

<sup>2</sup> V. Meyer and Langer, *Ber.*, 1882, **15**, 2769. See also *Pyrochemische Untersuchungen*, Braunschweig, 1885.

<sup>3</sup> Deville and Troost, *Compt. rend.*, 1867, **64**, 273.

<sup>4</sup> Naumann, *Ber.*, 1878, **11**, 2045.

<sup>5</sup> E. and L. Natanson, *Ann. Physik. u. Chem.* (3), 1885, **24**, 454; 1888, **27**, 606.

<sup>6</sup> Lemoine, *Ann. Chim. Phys.* (5), 1877, **12**, 145.

A further example of dissociation increasing with the temperature was given previously (p. 114), namely, the decomposition of amylene hydrobromide into its two components, as shown by the investigations of Würtz.

A dissociation process, which has been used from the most remote times for producing quicklime, is the decomposition of calcium carbonate,  $\text{CaCO}_3$ , into quicklime,  $\text{CaO}$ , and carbon dioxide,  $\text{CO}_2$ . This process was studied by Debray.<sup>1</sup> In this case we have a so-called heterogeneous equilibrium with two solid phases ( $\text{CaCO}_3$  and  $\text{CaO}$ ) and one gaseous phase ( $\text{CO}_2$ ).<sup>2</sup> The gaseous phase consists of one kind of molecules only, and just as is the case in the evaporation of a liquid, for instance water, thermodynamics requires that at a given temperature the pressure of the gas (here  $\text{CO}_2$ ) shall have a definite value. At  $440^\circ \text{ C.}$ , this pressure ( $p$ ) is inappreciable, at  $610^\circ \text{ C.}$  it is  $4\cdot 6 \text{ cm.}$ , at  $745^\circ \text{ C.}$   $28\cdot 9 \text{ cm.}$ , and at  $865^\circ \text{ C.}$   $133\cdot 3 \text{ cm. Hg}$  (according to Le Chatelier).

Thermodynamics requires for this case that—

$$\frac{d \log_e p}{dt} = \frac{W}{1\cdot 99 T^2}$$

where  $W$  is the heat of dissociation, and  $T$  the absolute temperature. A calculation of  $W$  from the dissociation pressures at  $745^\circ \text{ C.}$  and  $865^\circ \text{ C.}$ , using the above equation, gives  $W = 29,300 \text{ cal.}$  ( $29,750 \text{ cal.}$  according to Debray's data), which is in very good agreement with the value found directly, namely  $30,800 \text{ cal.}$  (according to Favre and Silbermann).

So-called molecular compounds of salts with water or ammonia behave in exactly the same way. Delbray<sup>3</sup> investigated, for instance, the vapour-pressure of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . This pressure

<sup>1</sup> Debray, *Compt. rend.*, 1867, **64**, 603. Cf. Le Chatelier, *Compt. rend.*, 1886, **102**, 1243.

<sup>2</sup> An equilibrium between substances in a homogeneous system is usually termed a "homogeneous equilibrium." The corresponding name for equilibrium in a heterogeneous system is "heterogeneous equilibrium." Gibbs called the homogeneous parts of a heterogeneous system the "phases" of that system. In the equilibrium between ice, water, and water-vapour at  $0^\circ \text{ C.}$ , there are three phases—one solid (ice), one liquid (water), and one gaseous (water-vapour).

<sup>3</sup> Debray, *Compt. rend.*, 1868, **66**, 194.

was constant as long as there was more water than corresponds to the formula  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . If the quantity of water sank below this, the pressure became much less.  $\text{Na}_2\text{HPO}_4$  crystallizes with  $12\text{H}_2\text{O}$  at low, and with  $7\text{H}_2\text{O}$  at high temperature. The vapour-pressure are given in the following table:—

Temp.	= 12·3	16·3	20·7	24·9	31·5	36·4	40·0
$\text{Na}_2\text{HPO}_4 + 7 - 12\text{H}_2\text{O}; a =$	7·4	9·9	14·1	18·2	30·2		
$\text{Na}_2\text{HPO}_4 + 0 - 7\text{H}_2\text{O}; b =$	4·8	6·9	9·4	12·9	21·3	30·5	41·2
Water	$c = 10·64$	13·77	18·13	23·38	34·33	45·13	54·86
	$\frac{a}{c} =$	0·71	0·72	0·78	0·78	0·88	
	$\frac{b}{c} =$	0·46	0·50	0·52	0·55	0·62	0·68
							0·75

If a salt-crystal (with water of crystallization) has a higher vapour-pressure than the vapour-pressure of the surrounding atmosphere, it loses its water of crystallization, which phenomenon is called efflorescence. On the other hand, if the vapour-pressure of the atmosphere is higher than that of the saturated solution of the salt, the salt absorbs water from the air and dissolves in it; such salts are said to be deliquescent.

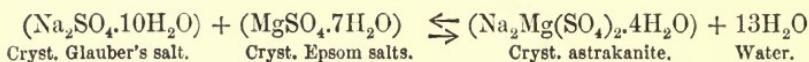
As will be seen from the above figures, the relative values of the vapour-tensions of the two salts  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , compared with that of pure water, increase steadily with the temperature. At about  $52^\circ\text{ C.}$   $\frac{a}{c}$  will reach the

value 1, and at about  $65^\circ\text{ C.}$   $\frac{b}{c}$  will reach this value. At higher

temperatures  $\frac{a}{c}$  (above  $52^\circ$ ) and  $\frac{b}{c}$  (above  $65^\circ$ ) would be greater than 1, *i.e.* the salts would have a greater vapour-tension than water. At temperatures above  $52^\circ\text{ C.}$ , if a crystal of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were placed near to, but not in contact with, a drop of water, water would distil from the crystal where the vapour-pressure is higher, to the water-drop where it is lower. In other words, the crystals of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  would not be stable above  $52^\circ\text{ C.}$ , but would lose water and form  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . (In reality they melt at a lower temperature,  $35^\circ\text{ C.}$  according to Tilden.) In the same way crystals of the latter salt are stable only up to  $65^\circ\text{ C.}$ , above which temperature anhydrous  $\text{Na}_2\text{HPO}_4$  is alone stable.

This is a common characteristic of all salts containing water of crystallization. On raising the temperature they give off moisture and form combinations with less water of crystallization, until finally the anhydrous salt is left. This simple process is often complicated by the crystals melting.

This is only a special case of the equilibria in so-called "condensed systems."<sup>1</sup> Such a system is—



This system has a so-called transition point at 21° 5 C. Below this temperature Glauber's salt and Epsom salts may coexist in contact with their saturated solution in water; at higher temperatures they are transformed into astrakanite and water.

The simplest of such condensed systems is the equilibrium between water and ice. At ordinary pressures the latter substance is stable below 0° C., and the former above this temperature. Therefore we conclude that the vapour-pressure of ice is lower than that of water at temperatures below 0° C., and that at higher temperatures the inverse is true, although this latter cannot be proved, since ice cannot be heated above 0° C., as Carnelley once thought he had been successful in doing. The following figures give the vapour-pressure of ice and water at temperatures below 0° C., according to Juhlin's, Marvin's, and Regnault's<sup>2</sup> measurements:—

#### ICE.

Temp. . . . .	-30	-20	-10	0° C.
Vapour-pressure . . . . .	0·292	0·787	1·974	4·579 mm.
W <sub>1</sub> : 18 . . . . .	672	673	666	cal.

#### WATER.

Temp. . . . .	-20	-10	0	+10	+20	+30	+40° C.
Vapour-pressure . . . . .	0·960	2·159	4·579	9·179	17·406	31·55	54·91 mm.
W <sub>1</sub> : 18 . . . . .	595	595	592	585	582	580	cal.

<sup>1</sup> Systems in which solutions or mixtures of gases play an unimportant rôle are called "condensed systems," a name given to them by van't Hoff.

<sup>2</sup> Cf. Scheel, *Verhand. Phys. Ges.*, 1905, 7, 391.

Now, for the vapour-pressure over ice ( $p_1$ ) we have—

$$\frac{d \log_e p_1}{dt} = \frac{W_1}{1.99T^2},$$

and for the vapour-pressure over water ( $p$ )—

$$\frac{d \log_e p}{dt} = \frac{W}{1.99T^2}$$

where  $W_1$  and  $W$  are the latent heats of evaporation of 1 gram-molecule (18 grams) of ice and of water respectively. From this it follows that—

$$\frac{d \log_e \frac{p_1}{p}}{dt} = \frac{W_1 - W}{1.99T^2} = \frac{Q}{1.99T^2},$$

where  $Q = W_1 - W$  is the difference between the latent heats of evaporation of ice and water. This difference is evidently equal to the latent heat of fusion of ice, for we might evaporate the ice in such a way that we first melt it and then evaporate the water. The figures given above agree very well with this theory. They give  $Q = 668 - 595 = 73$  cal. for a temperature of  $-10^\circ$  C., whereas different investigators have found the values 79.7 cal. at  $0^\circ$ , and 75 cal. at  $-10^\circ$  C. by direct calorimetric measurements.

Winkelmann and Dieterici, using calorimetric methods, have found the latent heat of evaporation of water to be 589.5 and 596.8 cal. respectively, whereas the figures given above correspond to 593 cal. At  $18^\circ$  C. Thomsen found, experimentally, 579 cal., so that the calculated value 584, given above, is probably a little too high.

In the same manner the heat of combination,  $Q$ , of  $\text{Na}_2\text{HPO}_4 \cdot 11\text{H}_2\text{O}$  with one molecule of liquid water to form the salt  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is given by the relation—

$$\frac{Q}{1.99T^2} = \frac{d \log_e \frac{a}{c}}{dt}.$$

The heat of combination,  $Q_1$ , of one molecule of water with  $\text{Na}_2\text{HPO}_4 \cdot 6\text{H}_2\text{O}$  is given by—

$$\frac{Q_1}{1.99T^2} = \frac{d \log_e \frac{b}{c}}{dT}.$$

We thus find  $Q = 1575$  cal. and  $Q_1 = 3105$  cal. The later determinations by Frowein<sup>1</sup> have given the calculated value of  $Q = 2240$ . Thomsen has found  $Q = 2238$  and  $Q_1 = 3015$ .

As an example of a salt combined with ammonia, the researches of Isambert<sup>2</sup> on the vapour-pressure of  $\text{AgCl} \cdot 3\text{NH}_3$  may be cited. They gave—

Temp.	0.3	12.9	18.8	22.6	25.3	27.9	31.0	34.2	48.5	57.0	°C.
Pressure of $\text{NH}_3$	300	500	700	900	1100	1300	1500	1713	2414	4880	mm.

The results of Jarry, mentioned on p. 70, give values for  $Q$  of 5824 and 4082 cal. for the dissociation of  $\text{AgCl} \cdot 3\text{NH}_3$  and  $2\text{AgCl} \cdot 3\text{NH}_3$  respectively. The data are—

for $\text{AgCl} \cdot 3\text{NH}_3$ .		for $2\text{AgCl} \cdot 3\text{NH}_3$ .	
$t$	$p$	$t$	$p$
-16	61 mm.	0	12 mm.
0	262	9.4	20
8	444	13	26
12.6	584	20	50
15	667	28	84
18	788	36.8	150
24	1090	41.5	202

A large number of such compounds of salts with water and ammonia have been examined by Horstmann, Wiedemann, Pareau, Lescoeur, Müller-Erzbach, and by van't Hoff and his students.

Here we touch the difficult question as to how the molecules of ammonia or water are bound in these complexes (see p. 85). The researches on the conductivity of such complexes in solution, especially those carried out by Werner and Miolati,<sup>3</sup>

<sup>1</sup> Frowein, *Zeit. physikal. Chem.*, 1887, **1**, 362.

<sup>2</sup> Isambert, *Compt. rend.*, 1868, **66**, 1259.

<sup>3</sup> Werner and Miolati, *Zeit. physikal. Chem.*, 1893, **12**, 35; 1894, **14**, 506; 1896, **21**, 225.

seem to indicate that the ammonia is bound to the positive ion, which may thus be regarded as a derivative of ammonium.

We have already considered some cases of heterogeneous equilibrium, in which the substances exist in different phases. The simplest case of such an heterogeneous equilibrium is that which exists at 0° C. between ice, water, and water-vapour, the pressure of the vapour being 4·6 mm. There are thus three phases, one solid (ice), one liquid (water), and one gaseous (vapour). For these Gibbs has enunciated his *phase rule*— $n$  different bodies (chemical substances, simple or compound) can form  $n + 2$  phases, and these can coexist at *one* single point only, *i.e.* at a definite temperature and pressure. This rule may easily be deduced in the following manner: For a gas we have the equation of condition,  $p = RTc$ , expressing the relation between its pressure,  $p$ , temperature,  $T$ , and concentration,  $c$ . Similarly, we have equations of condition for liquids and solids, although they are not so simple in these cases. If the three water-phases exist together, all three equations must hold, containing only three independent and unknown quantities, namely, pressure,  $p$ , temperature,  $T$ , and the concentration  $c$  of vapour, water, and ice. The three concentrations are not independent of each other, for as soon as the one is known the other two are thereby determined. Hence, there exists only one point where the three phases can coexist, namely, at 0° C. and 4·6 mm. pressure.

If we take only two phases, for instance, water and vapour, we may give any value to one of the variables, but then the other two also become fixed. Thus, for instance, at a given temperature the vapour-pressure is also given, and for this temperature the densities of the vapour and water have certain definite values. If there is only one phase, for instance, water-vapour, two variables, say temperature and pressure, may be arbitrarily chosen, but then the third variable, the concentration, becomes fixed, and its value may be calculated from the equation of condition.

The connection between the concentration of one of the substances, for instance, water, in one phase (*e.g.* the liquid) and its concentration in a second phase (*e.g.* the vapour) is expressed by a relation showing the work which is necessary to transfer a small quantity of water from the one phase into

the other. This work depends on the concentration, and at the equilibrium point is zero.

Similarly, if we have two substances ( $n = 2$ ), *e.g.* sodium chloride and water, we have four independent variables, namely, temperature, pressure, and the concentration of each of the substances in *one* of the phases. The same condition holds, namely, that if the concentration of one substance in one of the phases, *e.g.* of the salt in the liquid phase, is known, its concentration in all the other phases can be determined. Four ( $= n + 2$ ) phases may coexist, but only at one definite temperature, namely,  $-21.3^{\circ}\text{C}$ . These four phases are—water-vapour at  $0.73\text{ mm}$ . pressure; liquid, containing 36 grams of salt to 100 grams of water; ice; and solid crystals of the salt,  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ .

If the number of phases is diminished, *e.g.* if the solid salt is taken away, it is possible to choose one of the variables arbitrarily, *e.g.* the temperature (between  $0^{\circ}$  and  $-21.3^{\circ}\text{C}$ .), but then the other variables become fixed, so that the composition of the solution and the pressure of the saturated vapour can only have a certain definite value.

If there are only two phases, *e.g.* the liquid and the gaseous, we may arbitrarily choose two variables, *e.g.* temperature and concentration, but then the other two, the pressure of the vapour and its concentration, become fixed.

The phase rule of Gibbs is of great value for finding the number of possible combinations of any number of substances under any given external conditions.

## CHAPTER XII

### *OSMOTIC PRESSURE. GENERAL LAWS FOR DISSOLVED SUBSTANCES*

IN the year 1883 I carried out an investigation on the conductivities of different electrolytes,<sup>1</sup> and was thereby led to the conclusion that all the molecules of an electrolyte do not conduct the electric current. The molecules were, therefore, divided into two classes, active and inactive. At high dilutions all the molecules were supposed to be transformed into the active state. The number of electrically active molecules in a solution (*e.g.* of an acid) was measured by its conductivity.

Now, the order of different acids, as regards their power of displacing one another from their salts, was known from thermochemical measurements. This order was exactly the same as that of their conductivities in equivalent solutions. This circumstance led me to suppose that chemically active molecules are identical with electrically active ones, and therefore the conductivity of an acid was regarded as a measure of its strength. In consequence, it was argued that the velocity of a reaction, which may be brought about by different acids, is proportional to the conductivity of the acid used. I had very few figures for proving this law experimentally, but Ostwald soon after tested it, using the abundant material he had collected in his researches on velocities of reaction; the test was made more complete by measurements of the conductivities of the acids used. His research resulted in a complete verification of the law.

Generally speaking, there seems to be a certain parallelism

<sup>1</sup> Arrhenius, *Bihang till Kongl. Svenska Vet. Akad. Handlingar*, **8**, Nos. 13 and 14 (1884).

between electrical conductivity and chemical reactivity. Gore<sup>1</sup> found that pure anhydrous hydrochloric acid does not (appreciably) attack oxides and carbonates; also it is practically a non-conductor of electricity. Similarly, one can understand why concentrated sulphuric acid may be transported in iron vessels, whereas diluted sulphuric acid attacks them very rapidly.

The active molecules of the electrolytes were supposed to correspond to the molecules which, according to the hypothesis of Clausius, are exchanging their ions.

In 1885 van't Hoff<sup>2</sup> published a memoir on the analogy between the gaseous and the dissolved state of matter. Before this time it was known that substances in very dilute solutions show regularities which remind one of the behaviour of gases. Thus, for instance, we find some general remarks on this matter in the works of Horstmann and Jul. Thomsen. But van't Hoff was the first to throw a clear light on this subject.

Raoult<sup>3</sup> had found, that on dissolving different substances in the same solvent, the freezing-point of the solvent is lowered proportionally to the number of molecules dissolved in 100 grams of the solvent. He represented his results by the expression—

$$dt = 0.63n$$

where  $dt$  represents the lowering of the freezing-point in degrees C., and  $n$  the number of gram-molecules dissolved in 100 grams of the solvent. The results obtained with water as solvent were not in good agreement with this equation. Later on van't Hoff showed that Raoult's equation was not correct.

On the other hand, Raoult<sup>4</sup> found that the vapour-pressure  $p$  of a solvent was lowered to  $p_1$  on dissolving one gram-molecule of a non-volatile substance in  $N$  gram-molecules of the solvent. These quantities were connected with each other by the following simple law :—

$$\frac{p - p_1}{p} = \frac{1}{N}.$$

<sup>1</sup> Gore, *Proc. Roy. Soc.*, 1865, **14**, 204.

<sup>2</sup> Van't Hoff, *Kongl. Svenska Vet. Akad. Handlingar*, **21** (1885); *Zeit. physikal. Chem.*, 1887, **1**, 481.

<sup>3</sup> Raoult, *Compt. rend.*, 1882, **94**, 1517; **95**, 1030; *Ann. chim. phys.*, 1883, **28**, 137.

<sup>4</sup> *Ibid.*, 1885, **103**, 1125; 1887, **104**, 976 and 1430.

This law was afterwards found to be exact; it was because of its great simplicity that Raoult was enabled to discover it on purely experimental grounds.

Guldberg<sup>1</sup> had already, in 1870, from thermodynamical considerations, deduced the connection between the lowerings of the vapour-tension and of the freezing-point. If Raoult had been cognizant of Guldberg's work he would have been able to deduce the correct law for the freezing-point. However, being unaware of the previous theoretical work, he only established the fact that there was proportionality between the two lowerings (1878). Later on he also found proportionality between these lowerings and the rise in the boiling-point of a solvent produced by dissolving a non-volatile substance in it.

Finally, the plant-physiologists had drawn attention to the power possessed by cells of sucking in pure water from a sur-

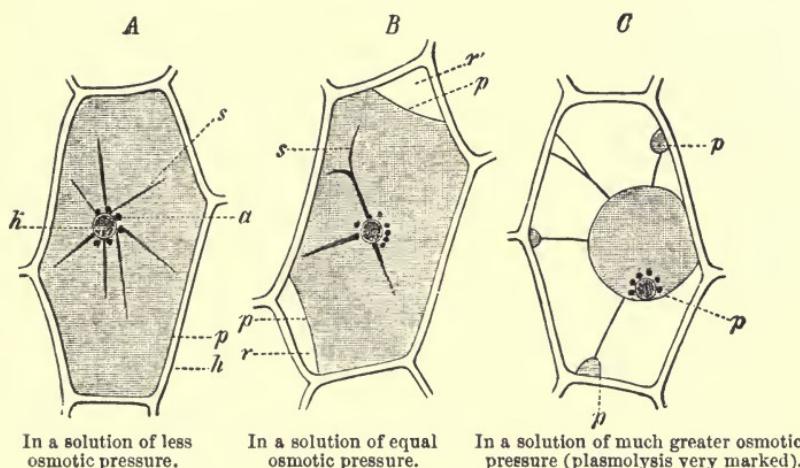


FIG. 18.—Plant cells, according to De Vries.

rounding weak salt solution. When this solution reached a certain concentration, equilibrium was established, and no water entered into the cells. The solution and the cell-content were then said to be "isotonic." If the solution were still more concentrated, water passed from the cells to the solution; the protoplasm contracted and did not fill out the surrounding cell-wall (see Fig. 18, A, B, C.). This could be observed under the

<sup>1</sup> Guldberg, *Compt. rend.*, 1870, **70**, 1349.

microscope, especially if the protoplasm was stained with a colouring matter—for instance, methyl-violet.

De Vries,<sup>1</sup> on examining this property, found that the same cells are isotonic with solutions containing the same number of molecules of salt to the litre, the salt being composed of two monovalent ions, *e.g.* potassium chloride, potassium nitrate, and sodium chloride or nitrate. Solutions of cane-sugar or of glycerine contained 1·7 times as many molecules as the corresponding solutions of the binary salts which were isotonic with the same cells. On the other hand, such salts as  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{K}_2\text{SO}_4$  had in equimolecular concentrations a greater effect than the salts of the type  $\text{KCl}$ . De Vries (1884) called attention to the fact that solutions isosmotic with the same cells possess the same freezing-point and vapour-pressure.

Donders and Hamburger,<sup>2</sup> using red blood-corpuscles, carried out researches similar to those of De Vries on plant-cells. If the solution surrounding the red blood-corpuscles is too weak, they give up their colouring matter, the hæmoglobin, to the solution. When this is too strong, the red blood-corpuscles shrink and sink to the bottom. In this way Donders and Hamburger determined the solutions which corresponded to each other, and found results wholly in accordance with those of De Vries.

Already in 1867 the German physiologist Traube<sup>3</sup> had succeeded in producing artificial cells possessing the osmotic properties of living ones. He found that membranes which are formed at the boundaries of two solutions, *e.g.* between solutions of gelatine and tannic acid, or between solutions of ferric chloride and potassium ferrocyanide, are permeable to water, but not to many substances dissolved in the water, as, for instance, potassium ferrocyanide and barium chloride. These membranes were, however, very unstable. Subsequently Pfeffer<sup>4</sup> deposited a membrane of copper ferrocyanide in a porous pot in the following manner: He took a porous earthenware pot and sucked water through it till the pores were

<sup>1</sup> De Vries, *Pringsheims Jahrb.*, 1884, **14**, 427.

<sup>2</sup> Donders and Hamburger, *Onderz. Physiol. Lab. Utrecht* (3), **9**, 26.

<sup>3</sup> Traube, *Arch. f. Anatomie u. Physiologie*, 1867, **87**.

<sup>4</sup> Cf. Pfeffer, "Osmotische Untersuchungen." Leipzig : 1877.

quite free from air. It was then filled with a solution of potassium ferrocyanide, and placed in a bath of copper sulphate. The two solutions diffused slowly into the walls of the cell, and where they met a thin film of colloidal ferrocyanide of copper was precipitated. This film increased in thickness the longer the two solutions were allowed to act upon one another. Such a cell showed a great similarity to living cells. It was semipermeable, that is, it allowed water to pass freely, whereas salts, cane-sugar, glycerine, etc., which were dissolved in the water, did not pass through the membrane of copper ferrocyanide. If the cell were filled with a solution of cane-sugar and put into water, the latter was sucked in slowly.

Pfeffer filled the cell A (see Fig. 19) with the solution he wished to study, and afterwards closed it by a cover (L) fitted with a manometer (M), and placed it in a water-bath at constant temperature. The water entered into the cell and raised the column of mercury contained in the manometric tube. Mercury was poured into this in order to increase the pressure, until a point was reached at which no more water entered the cell. This limiting pressure is called the *osmotic pressure* of the solution in the cell. It balances the tendency of the water to enter. If it is exceeded, water is pressed out from the cell.

When Pfeffer filled the cell with different solutions of cane-sugar, he observed the following osmotic pressures at 14° C. :—

Percentage of sugar, c.	1	2	2·74	4	6	
Osmotic pressure, p.	535	1016	1513	2082	3075	mm. Hg.
Ratio, p : c . . . .	535	508	554	521	513	

The numbers in the last line indicate that the osmotic pressure is nearly proportional to the concentration of the solution ; this conclusion was drawn by Pfeffer.

He also made experiments with other solutes, such as gum

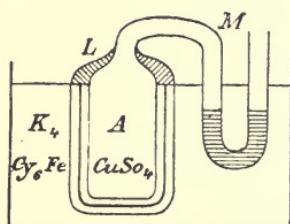


FIG. 19.—Measurement of osmotic pressure (Pfeffer).

arabic, dextrine, potassium sulphate, potassium nitrate, etc. For solutions of this last substance he found the following values of the osmotic pressure :—

Percentage of $\text{KNO}_3$ , $c.$	0·80	1·43	3·33
Osmotic pressure, $p.$	1304	2185	4368 mm. Hg.
Ratio, $p : c \dots \dots \dots$	1630	1530	1330

In this case the ratio is not quite constant, but sinks gradually with increasing pressure. Pfeffer showed this to be due to the fact that the membrane was not perfectly semi-permeable, especially at high pressures. The salt slowly passed through the membrane, although with a much less speed than the water. This is generally the case with such membranes ; the copper ferrocyanide membrane is the best of all those hitherto prepared (prussian blue, tannate of gelatine, etc.<sup>1</sup>).

Further, Pfeffer investigated the influence of temperature on osmotic pressure. He found that it increases slowly with the temperature, as the following figures for a one-per-cent sugar-solution indicate :—

Temperature . . .	6·8	13·5	14·2	22·0	32	36° C.
Osmotic pressure } (observed) . . .	505	521	531	548	544	567 mm. Hg.
Osmotic pressure } (calculated) . . .	505	517	518	532	551	559 ,,

The figures in the last line are calculated on the assumption that the osmotic pressure increases proportionately to the absolute temperature. The data are insufficient and too uncertain to prove the validity of such a law ; the observed increase between 6·8° and 36° C. is 1·16 times greater than that calculated.

The researches had advanced to this point when De Vries asked van't Hoff his opinion concerning the nature of osmotic pressure. Van't Hoff perceived the similarity of the laws for osmotic pressure and for gas pressure. Boyle's law indicates

<sup>1</sup> Cf. Morse and Horn, *Amer. Journ.*, 1901, **26**, 80; Berkeley and Hartley, *Proc. Roy. Soc.*, 1904, **73**, 436.

that the pressure of a gas is proportional to the concentration. This law was found by Pfeffer to be valid also for osmotic pressure, so long as the membrane was impermeable to the dissolved substance. Further, the pressure of a gas increases proportionately to the absolute temperature, and the osmotic pressure shows an increase of the same order of magnitude. An answer to the question whether Avogadro's law was also applicable to osmotic phenomena was still wanting. A cane-sugar solution containing one gram of cane-sugar in 99 grams of water occupies a volume of 99·7 c.c., and exerts a pressure of 505 mm. Hg at 6·8° C. = 279·8° abs. A solution of one gram-molecule (= 342 grams) cane-sugar in one litre would be 34·1 times more concentrated, and therefore have a pressure of 17,220 mm. Hg = 61·5 × 279·8. Therefore in this case R has the value 61·5, whereas for oxygen it is 62·39 (see p. 115). The two values are so very close that after this calculation van't Hoff did not hesitate to enunciate his important law, which is:—the osmotic pressure of a dilute solution, containing a definite quantity of dissolved matter, is just as great as the gas-pressure of this quantity of matter would be if it were distributed in the gaseous condition over the same volume at the same temperature.

Van't Hoff also indicated how the other phenomena which have been mentioned were connected with the osmotic pressure, *i.e.* how this could be calculated from the lowerings of the vapour-pressure and of the freezing-point.

The law of Raoult for the lowering of the vapour-pressure was found to be exact, but for the depression of the freezing-point the equation of Raoult was replaced by the following correct expression:—

$$dT = \frac{1\cdot99}{100} \cdot \frac{T^2}{W} \cdot n,$$

where  $dT$  is the lowering of the freezing-point,  $T$  its absolute temperature,  $W$  the heat of fusion of 1 gram of the solvent, and  $n$  the number of gram-molecules of the substance dissolved in 100 grams of the solvent. Eykman<sup>1</sup> showed by direct

<sup>1</sup> Eykman, *Zeit. physikal. Chem.*, 1889, 3, 203.

experiments that the equation of van't Hoff agrees with experiment, whereas that of Raoult often gives very incorrect results (cf. p. 158).

For the rise in the boiling-point the same equation is valid, but then W represents the heat of evaporation of 1 gram of the solvent.

By the help of these equations we may determine the molecular weights of all substances which can be dissolved in a solvent whose freezing-point or boiling-point is at an accessible temperature.

As examples of the laws mentioned, the following figures may be cited. The theoretical value for the relative lowering ( $l$ ) of the vapour-pressure of ethyl ether (mol. wt. = 74) on dissolving one gram-molecule (= M grams of a substance) in 1000 grams of ether is 0·074. The value found is—

	M.	$l$ .
Perchlorethane, $C_2Cl_6$ . . . . .	237	0·071
Methyl salicylate, $C_8H_8O_3$ . . . . .	152	0·071
Methyl azocuminate, $C_{22}H_{26}O_4N_2$ . .	382	0·068
Cyanic acid, $CNOH$ . . . . .	43	0·070
Benzoic acid, $C_7H_6O_2$ . . . . .	122	0·071
Trichloracetic acid, $C_2HO_2Cl_3$ . .	163·5	0·071
Benzaldehyde, $C_7H_6O$ . . . . .	106	0·072
Capryl alcohol, $C_8H_{18}O$ . . . . .	130	0·073
Cyanamide, $CN_2H_2$ . . . . .	42	0·074
Aniline, $C_6H_7N$ . . . . .	93	0·071
Mercury diethyl, $C_4H_{10}Hg$ . . . .	258	0·068
Antimony trichloride, $SbCl_3$ . . . .	228·5	0·067

The mean value is 0·071, in fairly good accordance with the theoretical one. Such mean values for different solvents, and calculated according to Raoult, are given in the following table. One gram-molecule was dissolved in one hundred gram-molecules of solvent. The theoretical value = 0·0100.

Solvent.	<i>l.</i>	Solvent.	<i>l.</i>
Water . . . . .	0·0102	Methyl iodide . . .	0·0105
Phosphorus trichloride	0·0108	Methyl bromide . . .	0·0109
Carbon disulphide . .	0·0105	Ethyl ether . . . .	0·0096
Carbon tetrachloride .	0·0105	Acetone . . . . .	0·0101
Chloroform . . . .	0·0109	Methyl alcohol . . .	0·0103
Amylene . . . . .	0·0106	Ethyl alcohol . . . .	0·0101
Benzene . . . . .	0·0106	Acetic acid . . . . .	0·0163

The deviations fall within the limits of experimental error, except in the case of acetic acid as solvent. But this exception proves the rule, for the molecular weight of acetic acid in the form of vapour, at the given temperature, is 1·62 times that calculated from its chemical formula, and the theory demands that the molecular lowering shall be greater in the same proportion.

The following table gives the mean of the molecular rise (*R*) in the boiling-point produced by the solution of one gram-molecule of a substance in 100 grams of solvent. Solutions of salts and organic acids are excluded.

	<i>R</i> <sub>obs.</sub>	Limits.	<i>R</i> <sub>calc.</sub>
Water . . . . .	5·0	4·8–5·3	5·2
Acetic acid . . . .	24·9	24·7–25·0	25·3
Ethyl alcohol . . .	11·1	10·3–11·8	11·5
Chloroform . . . .	35·6	34·5–36·2	36·6
Benzene . . . . .	25·5	24·4–27·2	26·7
Acetone . . . . .	—	17–18	16·7
Ethyl ether . . . .	—	21–22	21·1
Carbon disulphide .	—	22–24	23·7
Ethyl acetate . . .	—	25–26	26·0

The salts give too great a rise if they are dissolved in water, acids, or alcohol. This is due to electrolytic dissociation (see next chapter). The acids dissolved in benzene, chloroform, etc., give too low figures. They are therefore regarded

as giving complex molecules, just as they do in the gaseous state.

An extraordinarily large number of measurements of the molecular lowering ( $dT$ ) of the freezing-point have been made. Some figures of Eykman's are given below, which show the superiority of van't Hoff's law over Raoult's rule. The values calculated according to the two methods are indicated with an H and an R, and are written after the observed values.

Solvent.	$dT$ (obs.).	$dT$ (H).	$dT$ (R).
Phenol . . . . .	74	77·0	58·3
Naphthalene . . . . .	69	69·4	79·4
p-Toluidine . . . . .	51	49·0	66·3
Diphenylamine . . . . .	88	98·6	104·8
Lauric acid . . . . .	44	45·2	124·0
Palmitic acid . . . . .	44	44·3	158·7
Water . . . . .	17·7	18·6	11·3
Benzene . . . . .	49·3	53·0	49·1

The values  $dT$  give the lowering of the freezing-point on dissolving one gram-molecule in 100 grams of solvent.

For these determinations, which are of the highest interest to chemists, Beckmann<sup>1</sup> has constructed special forms of apparatus, which are now used in all chemical and physical laboratories. Many more molecular weights have been determined by measurements of boiling or freezing points, than with the aid of vapour-density determinations, and they all agree with van't Hoff's law—if we except solutions of electrolytes and the so-called solid solutions, which we shall consider later. Thus we may now say that van't Hoff's law has been found to be true wherever it has been applied, and it is the most general law of matter that we know.

That the vapour-pressure and the freezing-point bear an intimate relation to the osmotic pressure may be concluded from the fact that a vacuum or ice may be regarded as a

<sup>1</sup> Beckmann, *Zeit. physikal. Chem.*, 1888, 2, 638.

semipermeable membrane. Thus, if we have a solution and the solvent in two beakers standing side by side, and above them the saturated vapour, the solvent generally possesses a higher vapour-pressure than the solution, and therefore distils over to the solution. If the solute is not vaporizable, the space above both liquids is a semipermeable membrane, through which the solvent may pass, but not the solute. If the solute is volatile, the space is not completely semipermeable—just as, according to the experiments of Pfeffer, the copper ferrocyanide membrane is not wholly impermeable for the dissolved potassium nitrate—and deviations from the simple laws of Raoult and van't Hoff are observed.

In the same manner, we may figure to ourselves a vessel containing pure water and an aqueous solution of, *e.g.*, sodium chloride, separated by a wall of ice. We may now keep this vessel at a constant temperature, lying somewhere between the freezing-point of the water and the lower freezing-point of the solution. The water then freezes out on one side of the ice-wall, which melts on the other side, so that water diffuses into the solution. By choosing an appropriate temperature we may regulate this process so that just as much ice is melted on the one side as freezes out from the water on the other. We may therefore say that the ice acts as a semipermeable membrane, letting through water, but not the dissolved substance ( $\text{NaCl}$ ).

Here, also, some cases occur in which the solid wall of the frozen solvent is not wholly impermeable to the solute. This occurs with naphthalene as solvent, and  $\beta$ -naphthol as solute, or with tin as solvent and antimony as solute, or benzene as solvent and iodine as solute. The solid solvent then contains a homogeneous admixture of the solute, and the whole may be regarded as a solution of the solute in the solid solvent. Van't Hoff has examined these so-called "solid solutions" from this point of view, and deduced the same laws for them as for liquid solutions, so that in this case van't Hoff's law of the osmotic pressure is also valid for the solid state of matter.

If the solute has a measurable vapour-pressure, the total vapour-pressure is greater than it would be if the vapour-pressure of the solute were inappreciable. The total vapour-pressure is measured, and therefore the observed lowering of

the vapour-pressure is less than accords with Raoult's law. If the dissolved substance has a high vapour-pressure compared with that of the solvent, *e.g.* if alcohol is dissolved in water, it may happen that an increase in the vapour-pressure instead of a lowering is observed.

Similarly, if the solute enters into solution in the solid solvent, the observed lowering of the freezing-point is less than van't Hoff's law demands, and it sometimes happens that the freezing-point rises instead of falls.

But these apparent exceptions to the laws of van't Hoff and Raoult are easily explained, and have little importance compared with the exceptions shown by the solutions of electrolytes (salts, strong acids and bases). These all give a greater lowering of the freezing-point than that calculated according to van't Hoff's law. It is not possible to give an explanation by assuming the existence of solid solutions, any more than by assuming that complexes are formed in the solution by the molecules aggregating together, for in both these cases the observed lowering of the freezing-point should then be less than the calculated one.



## CHAPTER XIII

### *ELECTROLYTIC DISSOCIATION*

ELECTROLYTES in solution behave similarly to substances with too high vapour-pressure, for instance,  $\text{NH}_4\text{Cl}$ , the behaviour of which was explained by assuming that they are dissociated to a certain extent. Hence, we might try to explain these exceptions to van't Hoff's law by the assumption of a partial dissociation. We have seen that the molecules of electrolytes contain two kinds of molecules, inactive and active, and that the latter are characterized by an exchange of their ions, which recalls the phenomenon of dissociation. It is possible to calculate the number of the active molecules in a solution, *e.g.* a normal solution of sodium chloride, by comparing the conductivity of a gram of  $\text{NaCl}$  in it with the corresponding conductivity at a very high dilution. The quotient gives the relative number of active  $\text{NaCl}$  molecules, or, as we might also say, the degree of dissociation. This degree of dissociation is, if calculated from the measurements of Kohlrausch,<sup>1</sup> found to be 0·75. If we proceed in this way, we must therefore suppose that the solution of  $\text{NaCl}$  contains only 0·25 gram-molecule of  $\text{NaCl}$ , and 0·75 gram-molecule of  $\text{Na}$ , and an equivalent quantity of gram-molecules of  $\text{Cl}$ , making in all 1·75 gram-molecules. Now, the freezing-point of a normal solution is, according to van't Hoff's equation,  $-1\cdot85^\circ \text{ C.}$  We should, therefore, expect to find a lowering of the freezing-point of water ( $0^\circ \text{ C.}$ ) 1·75 times greater than that calculated, that is,  $1\cdot75 (-1\cdot85) = -3\cdot26^\circ \text{ C.}$  This, as a matter of fact, is exactly the freezing-point of a normal solution of  $\text{NaCl}$ .

<sup>1</sup> Kohlrausch, *Ann. Physik. u. Chem.* (3), 1879, 6, 1.

In the same way I<sup>1</sup> examined (1887) solutions of all the substances for which Raoult had determined the freezing-point, and for which the conductivity was known. They were about ninety in number. In nearly all these cases I found a very good agreement between the calculated and the observed values of the freezing-points, which seemed to show that the electrolytically conducting substances are dissociated to a large extent in their aqueous solutions. In some few cases a divergence existed between the observed values of the freezing-point and the calculated values, derived from the electrical conductivity.

I<sup>2</sup> examined these exceptions more closely, with the result that, using the newly observed values, the agreement was as good as for the other solutions. (The same is also true for electrolytes dissolved in other solvents, and giving electrically conducting solutions.) Fig. 20 gives some values of the molecular depression of the freezing-point, and shows that at the concentration 0 the theoretical value is attained.

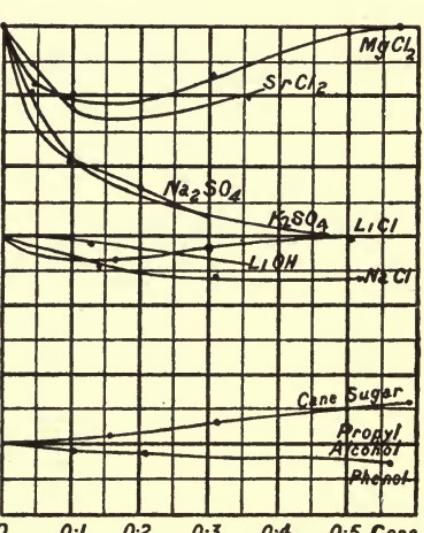


FIG. 20.—Molecular depression of the freezing-point.

case of substances exhibiting an "abnormally" high vapour-pressure, it has been shown that it is possible to partially separate their products of dissociation. Why does not an analogous experiment with dissociated electrolytes lead to the same result?

We may analyze this question a little more in detail. If a layer of pure water is placed over a solution of sodium chloride contained in a cylindrical vessel, the chlorine ions will, as Kohlrausch's figures for the conductivity show, diffuse about

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1887, **1**, 631.

<sup>2</sup> *Ibid.*, 1888, **2**, 491.

1·5 times more rapidly than the sodium ions. Therefore we may expect that after a short time there will be a slight excess of chlorine ions in the water above, and an equivalent excess of sodium ions in the solution below. Now, the ions carry their electrical charges with them, so that the water above should become charged negatively, and the solution below it positively. Because of this electric charge, the negative chlorine ions are held back, and the positive sodium ions attracted upwards from the solution, with a certain force. If the force driving the ions before the electric charge was called into existence is  $F$  (this force depends on the osmotic pressure of the ions), and the electric force is  $A$ , then the force driving the chlorine ions is represented by  $F - A$ , and that driving the sodium ions is  $F + A$ . As soon as  $F + A$  is 1·5 times greater than  $F - A$ , as many sodium ions as chlorine ions will enter the water above in unit time. It is not difficult to calculate the quantity of electricity and of chlorine ions, which are necessary for this effect. We find that (in a cylindrical vessel of 10 cm. height and 10 cm. in diameter) the billionth part of a milligram of chlorine ions is sufficient. By chemical analysis it will never be possible to detect this quantity, which, however, can be easily recognized by electrical means. It was exactly in this way that Nernst<sup>1</sup> calculated the electromotive force of concentration elements consisting of two differently concentrated solutions of the same salt between two unpolarizable electrodes. The electromotive force of certain concentration elements had already been calculated by Helmholtz<sup>2</sup> in 1881, from considerations based upon thermodynamics. Nernst's calculation agrees with that of Helmholtz, if in the equations which contain the vapour-pressure of the solutions this quantity is expressed as a function of the concentration, in accordance with the law of Raoult. The theoretical deduction of Nernst has the advantage over that of Helmholtz, that it is based upon easily manipulated kinetic considerations. On the other hand, that of Helmholtz is valid for all concentrations; that of Nernst only for dilute solutions.

The objection referred to above probably hindered an earlier

<sup>1</sup> Nernst, *Zeit. physikal. Chem.*, 1888, **2**, 617; 1889, **4**, 129.

<sup>2</sup> Helmholtz, *Sitzungsber. d. Berl. Ak. d. Wiss.*, July, 1882; *Gesammelte Abh.*, II., 979.

acceptance of the hypothesis of a dissociated state of the electrolytes, to which, for instance, Valson and Bartoli inclined.

The combined theories of osmotic pressure and of electrolytic dissociation have found a wide-reaching application in the short time of their existence. This can easily be understood if we take into consideration that by means of the laws of osmotic pressure we are able theoretically to foresee the properties of all kinds of (not too concentrated) solutions, whereas formerly only gases (which play a far less important rôle than solutions) could be subjected to theoretical treatment by means of their equations of condition. By the introduction of the theory of electrolytic dissociation, the numerous electrical phenomena were brought into intimate connection with the general laws of matter, and with the laws of the velocity of reaction. The simultaneous introduction of these two theories in general chemistry covered so wide a field, that many authors were thereby caused to forget that a theoretical chemistry had previously existed. On the other hand, some scientists considered the development to be going on with too great a speed, and believed it possible to reject all the new ideas without feeling that they consequently lost the old solid groundwork of accepted fundamental conceptions.

Here I can only give a very short *résumé* of the new domains, which have been opened to theoretical treatment by means of these advances.<sup>1</sup>

The most general and wide-reaching of the consequences of the hypothesis of electrolytic dissociation is that the properties of a very dilute solution of an electrolyte ought to be additive, that is, equal to the sum of the properties of the solvent and of the different ions into which the electrolyte is decomposed.

Now, it is well known that such additive properties are also found to a great extent in the case of substances which cannot possibly be regarded as dissociated. Thus, for instance, the fundamental law of the conservation of matter, formulated by Lavoisier, says that the mass of a compound is exactly equal to the sum of the masses of its constituents. (In reality mass is

<sup>1</sup> Cf. the text-books of Ostwald, Nernst, Arrhenius, Cohen, Jones, Jahn, the lectures of van't Hoff, etc., in which the newer developments are fully treated.

the only absolutely additive property of matter.) The extremely accurate examination of this law by Landolt, who some few years ago believed that he had found some very small, but, nevertheless, not unimportant exceptions to it, have finally resulted in a perfect proof of the accuracy of Lavoisier's conceptions (see p. 14).

There are other such properties, which are only approximately additive; for instance, the molecular volume of a compound may be regarded as the sum of the atomic volumes of its components. This law was found by Kopp to hold approximately for organic compounds, their volumes being measured at the boiling-point, and by Schroeder for salts of analogous composition, as, for instance, the halogen compounds of the alkali metals. The peculiarity of an additive property is that the exchange of one atom for another, *e.g.* Na for K, is always accompanied by the same quantitative change in the property. To illustrate this the following figures of Schroeder for molecular volumes (*i.e.* volumes of a gram-molecule) at 20° C. may be used :—

KCl,	37·4	KBr,	44·3	KI,	54·0	Br — Cl =	6·9	I — Br =	9·7
NaCl,	27·1	NaBr,	33·8	NaI,	43·5	Br — Cl =	6·7	I — Br =	9·5
Diff.	10·3	Diff.	10·5	Diff.	10·5				

In this case, evidently, the atomic volumes of K and Na may be expressed by two numbers which differ by 10·4 units.

The specific gravities of aqueous solutions are closely connected with the molecular volumes of the substances in solution. As long ago as 1870, Valson<sup>1</sup> had found that for all salts (not only for those of analogous composition) the specific gravity of the aqueous solution is an additive property in regard to the constituent ions (he called them radicles). He found the same to hold for the surface tension of salt solutions, which property, in later times, has been more thoroughly investigated by Röntgen and Schneider,<sup>2</sup> who verified the results of Valson. The latter was so strongly impressed by these regularities, that

<sup>1</sup> Valson, *Compt. rend.*, 1871, **73**, 441; *Ann. chim. phys.* (4), 1870, **20**, 361.

<sup>2</sup> Röntgen and Schneider, *Ann. Physik. u. Chem.* (3), 1886, **29**, 202.

he expressed the view that in this connection salt molecules behaved as if they were dissociated into their ions ("radicles").

As an instructive example of an additive property of solutions, where the additivity is evidently due to electrolytic dissociation, the relative compressibilities of 0·7 normal solutions of different salts, according to the measurements of Röntgen and Schneider,<sup>1</sup> may be cited. The compressibility of water is taken as 1000 units. The relative apparent compressibilities at 18° C. are—

	H	$\Delta$	NH <sub>4</sub>	$\Delta$	Li	$\Delta$	K	$\Delta$	Na
I . . .	—	—	954	14	940	8	932	8	924
NO <sub>3</sub> . .	981	27	954	20	934	4	930	8	922
Br. . .	981	28	953	19	934	4	930	7	923
Cl . . .	974	29	945	17	928	9	919	2	917
OH . . .	1000	(8)	992	(97)	895	11	884	3	881
SO <sub>4</sub> . . .	970	(117)	853	(40)	813	9	804	1	803
CO <sub>3</sub> . . .	—	—	—	—	—	—	798	1	797
Mean . .		28		18		7		5	

In the vertical columns the compressibilities of the different compounds of the same positive ion are given. Under  $\Delta$  the differences between the two neighbouring columns are tabulated. As is well known from electrical measurements, the molecules of water, and also of ammonia at this concentration, are dissociated only to a very slight degree (less than 1%); sulphuric acid is dissociated to about 50%, the sulphates and carbonates to about 60, the other salts to about 75, the other bases to about 80, and the other acids to about 82%. The additive scheme given above agrees best for the three monovalent acids, their salts and the bases, except ammonia. The greatest deviation from the mean is here 3 to 4 units (the mean difference is 2 units). The agreement is not nearly so good for the sulphates and carbonates; the greatest deviation is 22, the mean 8, units. Very great deviations, amounting to 89, 79, and 20 units, are found for the

<sup>1</sup> Röntgen and Schneider, *Ann. Physik. u. Chem.* (3), 1886, 29, 185.

three remaining least dissociated compounds, namely,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{N}$ , and  $\text{H}_2\text{O}$ .

Analogous remarks may be made regarding other properties of aqueous solutions of different electrolytes. Such properties are, for example, the molecular electrical conductivity (Kohlrausch), the internal friction (Arrhenius),<sup>1</sup> the molecular refraction (Gladstone),<sup>2</sup> the natural rotation of polarized light (Oudemans),<sup>3</sup> the magnetic rotation of polarized light (Perkin<sup>4</sup> and Jahn<sup>5</sup>) and the molecular magnetization (G. Wiedemann).<sup>6</sup>

The most important of these additive properties are those of which we make use in chemical analysis. All ferrous salts give the characteristic reactions of the ferrous ion, *e.g.* they are precipitated by alkali carbonates or hydrates, they give with potassium ferricyanide a blue precipitate (Turnbull's blue), and so on; but this is not true for potassium ferrocyanide, which was formerly regarded as a ferrous salt. This is due to the circumstance that the ferrocyanides do not contain the positive ferrous ion (to any appreciable extent), as was pointed out in my inaugural dissertation of 1883. Another still more instructive example was given by Ostwald. All true chlorides give a white flocculent precipitate with solutions of silver salts (the one most used is silver nitrate). It was therefore said formerly that silver salts are reagents for chlorine. Now we say that silver ions are reagents for chlorine ions. This formulation is better than the old one, for neither all silver salts (*e.g.* potassium silver cyanide and many other compounds of silver) nor all chlorine compounds (*e.g.* potassium chlorate and many organic chlorides) give this characteristic reaction.

The experiment succeeds only with such silver and chlorine compounds as are in a measurable degree decomposed into silver and chlorine ions. The theory requires that these ions shall be present in such quantities that the quantity of silver

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1887, **1**, 285.

<sup>2</sup> Gladstone, *Phil. Trans.*, 1868.

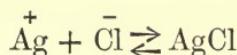
<sup>3</sup> Oudemans, *Beiblätter.*, 1885, **9**, 635.

<sup>4</sup> Perkin, *Journ. Chem. Soc.*, 1882-1889.

<sup>5</sup> Jahn, *Ann. Physik. u. Chem.* (3), 1891, **43**, 280.

<sup>6</sup> Wiedemann, *Ann. Physik. u. Chem.* (2), 1865, **127**, 1; 1868, **135**, 177.

chloride formed from them according to the equation of equilibrium—



shall exceed the soluble quantity of this salt.

Ostwald<sup>1</sup> has treated this and similar questions in detail, and has given an exposition of the general phenomena of analytical chemistry, which previously lacked an exact scientific foundation.

To this chapter belong, also, the poisonous and curative properties of certain salts; such an effect may be considered as a special physiological reaction of these salts. Thus, for instance, it has long been known that equivalent quantities of different potassium salts exert the same poisonous effect (if the accompanying negative ion is innocuous), and that equivalent quantities of different salts of quinine possess the same curative power. In these two cases the salts may without noticeable error be regarded as wholly dissociated into their ions, after they have been dissolved in the humours of the body. In other cases, as, for instance, for salts of mercury, the electrolytic dissociation is very small, and not the same for different salts, even at the great dilution in which they are present in the body. These cases have been treated with great success from the point of view of the electrolytic dissociation theory by Krönig and Paul,<sup>2</sup> Kahlenberg,<sup>3</sup> Loeb,<sup>4</sup> Clark,<sup>5</sup> and others.

A property which is of physical character, but is much used by the analytical chemist, is the colour of solutions. It has been subjected to a thorough investigation by Ostwald. To begin with, we will trace how a compound, *e.g.* fluorescein, C<sub>20</sub>H<sub>12</sub>O<sub>5</sub>, behaves if we replace its hydrogen atoms by other atoms, such as metals, halogens, or atomic groups such as NO<sub>2</sub>. The curves in Fig. 21 indicate the positions and strengths of the absorption bands in the absorption spectra of solutions of the

<sup>1</sup> Cf. Ostwald's "Scientific Foundations of Analytical Chemistry."

<sup>2</sup> Krönig and Paul, *Zeit. physikal. Chem.*, 1896, **21**, 414.

<sup>3</sup> Kahlenberg and True, *Bot. Gaz. Chicago*, 1896, **22**, 181; *Zeit. physikal. Chem.*, 1893, **12**, 473.

<sup>4</sup> Loeb, *Pflügers Archiv.*, 1897, **69**, 1; 1898, **71**, 457.

<sup>5</sup> Clark, *Jour. physikal. Chem.*, 1899, **3**, 263; 1901, **5**, 298.

corresponding compounds. A replacement of two atoms of hydrogen by two atoms of potassium in fluorescein itself (that is, the formation of a potassium salt from the acid) completely alters the absorption spectrum. Instead of a single absorption band in the blue for the acid, we find two absorption bands in the blue and the blue-green part of the spectrum for the salt. A similar observation may be made for tetraiodofluorescein (eosine) and its potassium salt. The reason of this is that both fluorescein and eosine are dissociated only to a slight

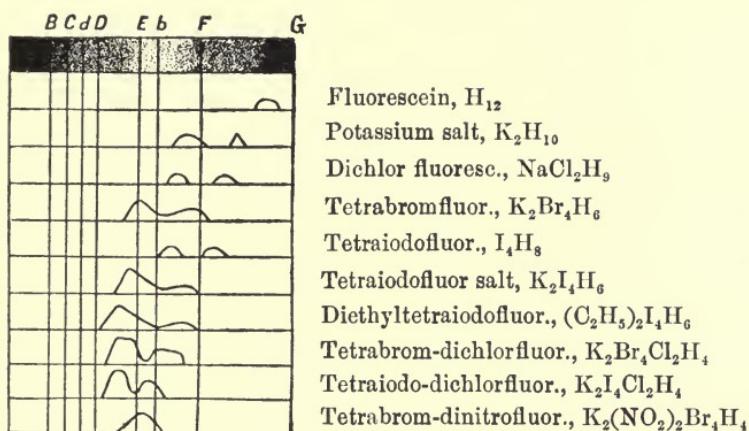


FIG. 21.—Absorption spectra of fluorescein derivatives (W. Vogel).

extent, so that their solutions give the absorption spectra of the respective compounds, and not of their negative ions ; the salts of the alkali metals, on the other hand, are almost completely dissociated into their ions at the high dilution used in these investigations, and therefore their solutions show the spectra of the negative ions (the ions of the alkali metals having no appreciable absorption in the visible part of the spectrum).

In general, exactly as in the two cases discussed, the figure shows that the absorption spectrum changes in a very marked manner with the smallest chemical change in the absorbing molecules.

It might therefore be expected, according to the old view, that the replacement of hydrogen by a metal in permanganic acid, or of a negative radicle by another in the salts of pararosaniline, would completely change the character of their

absorption spectra. This is not the case, as Ostwald<sup>1</sup> has shown. The spectra remain quite unchanged, as the next two figures (Figs. 22 and 23) show. Only in the case of pararosaniline salts do we observe that the absorption is sensibly weaker in some

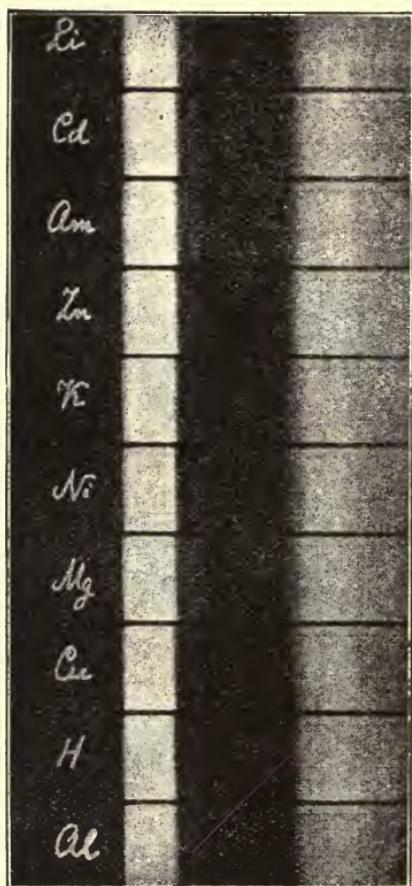


FIG. 22.—Absorption spectra of the permanganates (Ostwald).

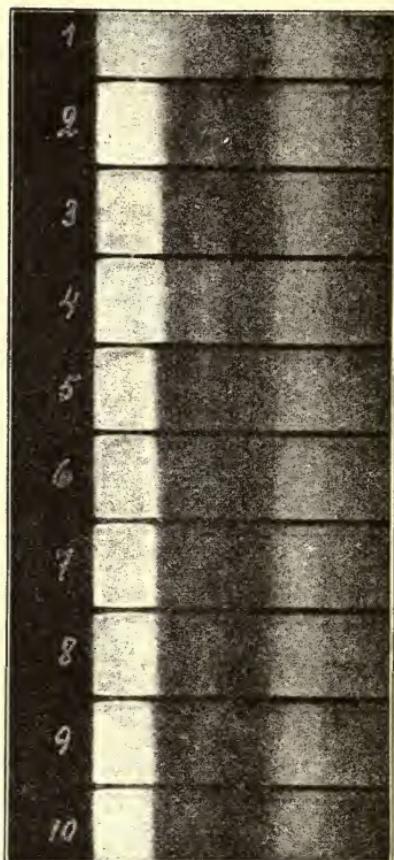


FIG. 23.—Absorption spectra of the rosaniline salts (Ostwald).

- |                       |                            |
|-----------------------|----------------------------|
| 1. Laevulinic acid.   | 6. Sulphanilic acid.       |
| 2. Acetic acid.       | 7. Nitric acid.            |
| 3. Chloric acid.      | 8. Phthalimidoacetic acid. |
| 4. Benzoic acid.      | 9. Butyric acid.           |
| 5. Hydrochloric acid. | 10. Phenyl propionic acid. |

cases than in others. The weakening depends on the hydrolysis of the salts of the weak acids, *e.g.* acetic and benzoic acid.

In these cases the dilution is extremely great (0·002 normal solutions of the permanganates and 0·00017 normal solutions of

<sup>1</sup> Ostwald, *Zeit. physikal. Chem.*, 1892, 9, 579.

the pararosaniline salts), so that the electrolytic dissociation of the electrolytes examined may be regarded as complete. Since the other ions present show no absorption, that which is observed in the solutions of all permanganates is the absorption due to the same quantities of the permanganate ion, and in the solutions of pararosaniline salts (in the cases where there is no appreciable hydrolysis) that due to the same quantities of the positive pararosaniline ion. The spectra belonging to each of these two groups must therefore be identical with each other. Observation has verified this, and the complete resemblance in every part of the spectrum may be used as a proof of the correctness of the dissociation theory.

In the same manner Ostwald investigated three other positive and twelve other negative ions, and obtained similar results. His research may therefore be regarded as one of the most convincing proofs of the correctness of the views used in the development of the theory of electrolytic dissociation.

The equilibrium between different gases may, as seen previously (p. 147), be calculated by the application of thermodynamics to the gas laws. As these laws are also found to be applicable to solutions, according to the researches of van't Hoff, it was natural to try if it were possible to calculate the equilibrium of dissociation between the molecules of an electrolyte and its ions. Ostwald<sup>1</sup> found that weak acids conform very closely to the requirements of the theory, so that if  $\text{H}^+$  and  $\bar{\text{A}}$  are the two ions of an acid  $\text{HA}$ , the following equation holds good :—

$$\text{Conc. of } \text{HA} = \text{const.} (\text{conc. of } \text{H}^+ \times \text{conc. of } \bar{\text{A}}).$$

To illustrate this, some figures of van't Hoff may be cited, which hold good for acetic acid at  $14^\circ\text{C}$ . In the table  $v$  represents the volume in which one gram-molecule (60 grams) of acetic acid is dissolved.  $\alpha_{\text{obs.}}$  is the fraction dissociated, calculated from the conductivity (cf. p. 169),  $\alpha_{\text{calc.}}$  is the corresponding quantity calculated according to the above equation, where  $K$  is put equal to  $17.8 \times 10^{-6}$ . Evidently the concentration of both the ions  $\text{H}$  and  $\text{CH}_3\text{CO}_2$  is the same in this case.

<sup>1</sup> Ostwald, *Zeit. physikal. Chem.*, 1888, **2**, 36.

<i>v</i>	100 <i>a</i> <sub>obs.</sub>	100 <i>a</i> <sub>calc.</sub>
0·994	0·402	0·42
2·02	0·614	0·60
15·9	1·66	1·67
18·9	1·78	1·78
1500	14·7	15·0
3010	20·5	20·2
7480	30·1	30·5
15000	40·8	40·1
$\infty$	100·0	100·0

As a matter of fact, the laws of equilibrium have found a much wider and better application in this branch of science than in the case of gases.

The weak bases, *e.g.* ammonia and its derivatives, behave in exactly the same manner, as Bredig<sup>1</sup> has shown. But the most strongly dissociated substances—salts, strong acids and bases—do not behave nearly so regularly. There is no doubt that at very high dilutions these substances follow the gas laws, but even in 0·01 normal solutions deviations from the simple laws are found, which thereby lose their practical value for calculations.

In this example we have considered the simplest case of equilibrium, where the two ions are present in the same concentrations. It is easy to introduce the one ion in excess; for instance, by adding an acetate to acetic acid. As follows from the above equation, the concentration of the H-ions will be reduced in nearly the same proportion as that of the acetate ions is increased, for in solutions of moderate dilution nearly all molecules of the acid remain undissociated, *i.e.* the concentration of the undissociated molecules HA remains nearly constant. By the aid of catalytic processes it is possible, as will soon be seen, to determine the concentration of the H-ions. The results of observations show a very good agreement with the calculation.<sup>2</sup>

Further, the general law of equilibrium between any given number of electrolytes is easily deduced in the same manner. A simple case of this general equilibrium has been treated

<sup>1</sup> Bredig, *Zeit. physikal. Chem.*, 1894, **13**, 289.

<sup>2</sup> Cf. Arrhenius, *Zeit. physikal. Chem.*, 1890, **5**, 1.

experimentally by Thomsen and Ostwald, and concerns the so-called avidity of acids. Equivalent quantities of two acids and one base are mixed; an equilibrium establishes itself between the two acids and the two possible salts. Their relative quantities may be determined in the manner described on p. 142. The proportion of the two salts formed is called the relative avidity of the two acids. For instance, if 100 c.c. of normal nitric acid and the equivalent quantities of dichloracetic acid and sodium hydrate are mixed with each other, 0·76 equivalent of sodium nitrate and 0·24 equivalent of sodium dichloracetate are found to be formed. The relative avidity of  $\text{HNO}_3$  and  $\text{CHCl}_2\text{COOH}$  is therefore said to be 0·76 to 0·24 = 3·17. I give here the measurements of Ostwald, carried out at 25° C. with normal solutions. The figures calculated from the conductivities of the respective acids and salts are given for comparison. The agreement is satisfactory.

			Obs.	Calc.
Nitric acid:	dichloracetic	acid	0·76 : 0·24	0·69 : 0·31
Hydrochloric acid:	"	"	0·74 : 0·26	0·69 : 0·31
Trichloracetic	"	"	0·71 : 0·29	0·69 : 0·31
Dichloracetic	"	lactic	0·91 : 0·09	0·95 : 0·05
Trichloracetic	"	monochloracetic	0·92 : 0·08	0·91 : 0·09
"	"	formic	0·97 : 0·03	0·92 : 0·08
Formic	"	lactic	0·54 : 0·46	0·56 : 0·44
"	"	acetic	0·76 : 0·24	0·75 : 0·25
"	"	butyric	0·80 : 0·20	0·79 : 0·21
"	"	isobutyric	0·79 : 0·21	0·79 : 0·21
"	"	propionic	0·81 : 0·19	0·80 : 0·20
"	"	glycollic	0·44 : 0·56	0·53 : 0·47
Acetic	"	butyric	0·53 : 0·47	0·54 : 0·46
"	"	isobutyric	0·53 : 0·47	0·54 : 0·46

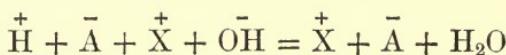
The theory leads to the result that the avidities of two acids stand to each other in the same proportion as their conductivities at the same degree of dilution.

At the point of equilibrium solid substances may separate out; in this case we take into consideration only the dissolved parts (cf. p. 140). This is, for instance, the case when one of the undissociated salts is very slightly soluble, e.g. silver chloride

(cf. p. 176). Van't Hoff,<sup>1</sup> Nernst,<sup>2</sup> Noyes<sup>3</sup> and others have examined this question and found experiment and theory to agree. In this case the product of the concentration of the two ions, the so-called solubility product, is constant.

In nature the most important rôle of all electrolytes is played by water, which may be regarded either as a very weak acid, for it contains  $\text{H}^+$ -ions, or as a very weak base, since it contains  $\text{OH}^-$ -ions. Therefore it partially displaces weak acids or bases from their salts, a phenomenon which is known as hydrolysis. In the waters of the ocean carbonates are partially hydrolyzed; this is also true for the carbonates, phosphates, and albuminates in the humours of the animal body, and for the carbonates and silicates in river waters which have washed the surface of the earth, as well as for those in the magma of the inner layers of the earth. These interesting questions have been investigated by Bodländer,<sup>4</sup> Sjöqvist,<sup>5</sup> myself<sup>6</sup> and others, and the application of the theory of electrolytic dissociation has thrown much light upon them.

For salts of strong acids and strong bases the hydrolysis is practically nil. In very dilute solutions the strong acids of the type  $\text{HA}$  are practically completely dissociated into their ions  $\text{H}^+$  and  $\bar{\text{A}}$ , and, similarly, the strong bases  $\text{XOH}$  are completely dissociated into their ions  $\text{X}^+$  and  $\text{OH}^-$ . On mixing equivalent quantities of a very dilute strong acid and a very dilute strong base, the following equation holds good:—



The two symbols  $\text{X}^+$  and  $\bar{\text{A}}$  together represent the salt, which is completely dissociated at high dilutions. The neutralization of a strong acid by a strong base corresponds to the formation of water from its component ions,  $\text{H}^+$  and  $\text{OH}^-$ . The process is

<sup>1</sup> Van't Hoff and Reicher, *Zeit. physikal. Chem.*, 1889, **3**, 484.

<sup>2</sup> Nernst, *Zeit. physikal. Chem.*, 1889, **4**, 372.

<sup>3</sup> Noyes, *Zeit. physikal. Chem.*, 1890-1895.

<sup>4</sup> Bodländer, *Zeit. physikal. Chem.*, 1881, **7**, 358.

<sup>5</sup> Sjöqvist, *Skand. Archiv. f. Physiologie.*, 1895, **5**, 317.

<sup>6</sup> Arrhenius, *Zeit. physikal. Chem.*, 1890, **5**, 19; 1894, **13**, 407.

independent of the nature of the acid and base used, and therefore the same quantity of heat (13,500 cal. at 18° C.) is always evolved on the neutralization of strong acids by strong bases, as Jul. Thomsen<sup>1</sup> found. The theory of electrolytic dissociation has thus furnished an explanation of this important law of thermochemistry.

If the acid and base used in the neutralization are not completely dissociated, the heat of neutralization is equal to the heat of formation of water (13,500 cal. at 18° C.) diminished by the quantities of heat which must be supplied to dissociate the undissociated parts of the acid and the base. By means of the formula given on p. 148, which van't Hoff has deduced, this quantity of heat may be calculated from the change in the electrical conductivity of aqueous solutions of the acid and the base with temperature. I<sup>2</sup> made the necessary measurements, and from them calculated the heats of neutralization of different acids by sodium hydrate, and compared these calculated values with those observed by Jul. Thomsen at 21°5 C. This comparison gives—

	Heat of neutralization.		
	Observed.		Calculated.
Hydrochloric acid	. . . . .	13,447	. . . 13,740
Hydrobromic	,, . . . .	13,525	. . . 13,750
Nitric	,, . . . .	13,550	. . . 13,680
Acetic	,, . . . .	13,263	. . . 13,400
Propionic	,, . . . .	13,598	. . . 13,480
Butyric	,, . . . .	13,957	. . . 13,800
Succinic	,, . . . .	12,430	. . . 12,400
Dichloracetic	,, . . . .	14,930	. . . 14,830
Phosphoric	,, . . . .	14,959	. . . 14,830
Hypophosphorous acid	. . . . .	15,409	. . . 15,160
Hydrofluoric acid	. . . . .	16,320	. . . 16,270

On neutralizing an acid with a base there is an increase in volume. Ostwald has measured this increase, which is called the "neutralization volume." As the theory demands, this

<sup>1</sup> Thomsen, cf. esp. *J. pr. Chem.* (2), 1876, **13**, 241; "Thermochemische Untersuchungen," vol. i. (Leipzig, 1882).

<sup>2</sup> Arrhenius, *Zeit. physikal. Chem.*, 1889, **4**, 96.

volume is found to be the same for the neutralization of all strong acids by strong bases at high dilutions, namely, 19·6 c.c. per gram equivalent. Thus, for instance, the volumes found for the following acids were :—

		Neutralization by	
		KOH	NaOH
Nitric acid, HNO <sub>3</sub>	. . . . .	20·0	19·8
Hydrochloric acid, HCl	. . . . .	19·5	19·2
Hydrobromic acid, HBr	. . . . .	19·6	19·3
Hydriodic acid, HI	. . . . .	19·8	19·5

The small differences which exist may be explained as being due partly to the electrolytic dissociation of the electrolytes used not being complete, and partly to errors of observation.

For the neutralization of weak acids by KOH and NaOH Ostwald found very different values. These might be calculated, if we knew the change of volume caused by the electrolytic dissociation of the undissociated molecules of these acids. This volume cannot be directly measured, but it can be calculated by means of an equation deduced by Planck<sup>1</sup> (cf. p. 148) from thermodynamics, giving the connection between the change in the conductivity of these acids and the pressure. Fanjung<sup>2</sup> determined experimentally the conductivity of different acids at different pressures (from 1 to 500 atm.), and from his figures calculated the neutralization-volume of the following weak acids. In the following table the calculated values are compared with the mean value for KOH and NaOH observed by Ostwald :—

Volume of neutralization.			
		Observed (Ostwald).	Calculated (Fanjung).
Formic acid	. . . . .	7·7 c.c.	8·7 c.c.
Acetic	„ . . . .	10·5 „	10·6 „
Propionic	„ . . . .	12·2 „	12·4 „
Butyric	„ . . . .	13·1 „	13·4 „
Isobutyric	„ . . . .	13·8 „	13·3 „
Lactic	„ . . . .	11·8 „	12·1 „
Succinic	„ . . . .	11·8 „	11·2 „
Maleic	„ . . . .	11·4 „	10·3 „

The agreement is satisfactory.

<sup>1</sup> Planck, *Ann. physik. u. Chem.* (3), 1887, **32**, 494.

<sup>2</sup> Fanjung, *Zeit. physikal. Chem.*, 1894, **14**, 673.

If we knew the change in the conductivity of water with the temperature, we could, in an analogous manner, making use of the equation of van't Hoff, calculate the heat of dissociation of water into its ions  $\text{H}^+$  and  $\text{OH}^-$ , which is identical with, but of opposite sign to, the heat of neutralization of strong acids by strong bases at high dilutions. Such determinations have been made by Kohlrausch and Heydweiller.<sup>1</sup> The observed values were compared with those calculated from the heat of dissociation of water, as determined by Thomsen's measurements of the heat of neutralization. This changes with the temperature, and in the interval investigated ( $-2^\circ$  to  $+50^\circ\text{C}$ .), it is approximately inversely proportional to the absolute temperature. Kohlrausch and Heydweiller give the following values for the specific conductivity ( $k$ ) of water, multiplied by  $10^6$  :—

Temp.	$10^6 k_{\text{obs.}}$	$10^6 k_{\text{calc.}}$
$-2^\circ\text{ C.}$	0·0107	0·0103
$+4$	0·0162	0·0158
10	0·0238	0·0236
18	0·0386	0·0386
26	0·0606	0·0601
34	0·0890	0·0901
42	0·1294	0·1305
50	0·1807	0·1839

The agreement is so excellent that Kohlrausch and Heydweiller regard it as the most convincing proof of the correctness of the theory of electrolytic dissociation. The degree of dissociation of water into its ions is so very small, that at  $0^\circ\text{ C.}$  only  $0·35 \times 10^{-7}$ , at  $25^\circ\text{ C.}$   $1·04 \times 10^{-7}$ , and at  $50^\circ\text{ C.}$   $2·48 \times 10^{-7}$  gram-ions of hydrogen ( $\text{H}^+$ ) are contained in one litre of water. For most purposes, as, for instance, in calculating the heat of neutralization, we may therefore, without noticeable error, neglect the dissociated parts of the water.

The electrolytic dissociation of water has been determined indirectly in three different ways, namely, from the hydrolysis of salts (avidity of water) by myself,<sup>2</sup> from the electromotive

<sup>1</sup> Kohlrausch and Heydweiller, *Zeit. physikal. Chem.*, 1894, **14**, 317.

<sup>2</sup> Arrhenius, *Zeit. physikal. Chem.*, 1893, **11**, 821.

force of different galvanic combinations of acids and bases (Ostwald<sup>1</sup>), and from its catalytic action in decomposing methyl-acetate (Wys<sup>2</sup>). These different methods give results which agree well with the measurements of Kohlrausch and Heyde-willer. Hence the theory is confirmed by all these different measurements.

Already at an early stage (1883), I<sup>3</sup> showed by theoretical considerations that the catalytic actions of different acids depended on their strength. "The strength of an acid" is only another expression for the H-ions contained in a given volume. Therefore, we should expect that the catalytic action, for instance, the velocity of reaction in the inversion of cane-sugar, would be proportional to the concentration of hydrogen ions present. This I was able to prove to be true, if a (small) correction was introduced for the so-called "salt-action," as the following figures indicate:—

Acid.	Concen-tration (molar).	Velocity of inversion.	
		Observed.	Calculated.
Hydrochloric acid, HCl	0·5	20·5	20·1
	0·1	3·34	3·41
	0·01	0·317	0·318
Hydrobromic „ HBr	0·5	22·3	22·2
	0·1	3·41	3·50
	0·01	0·318	0·324
Sulphuric „ H <sub>2</sub> SO <sub>4</sub>	0·25	10·7	11·1
	0·05	2·08	2·09
	0·005	0·265	0·256
Formic „ HCOOH	0·5	0·332	0·345
	0·1	0·135	0·134
	0·01	0·0372	0·0360
Acetic „ CH <sub>3</sub> COOH	0·5	0·1005	0·1005

<sup>1</sup> Ostwald, *Zeit. physikal. Chem.*, 1893, **11**, 521.

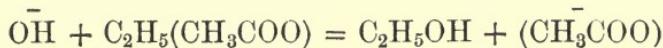
<sup>2</sup> Wys, *Zeit. physikal. Chem.*, 1893, **11**, 492; **12**, 514.

<sup>3</sup> Arrhenius, *Bihang. till. Svenska Vet. Akad. Handl.*, **8**, 14.

Acid.	Concen- tration (molar).	Velocity of inversion.	
		Observed.	Calculated.
Acetic acid, $\text{CH}_3\text{COOH}$	0·1	0·0430	0·0409
Propionic, $\text{C}_2\text{H}_5\text{COOH}$	0·5	0·0771	0·0750
" "	0·1	0·0341	0·0325
" "	0·01	0·0097	0·0095
Butyric, $\text{C}_3\text{H}_7\text{COOH}$	0·5	0·0791	0·0749
" "	0·1	0·0362	0·0355
" "	0·01	0·0100	0·0095
Succinic, $\text{C}_2\text{H}_4(\text{COOH})_2$	0·25	0·1210	0·1280
" "	0·05	0·0536	0·0531
" "	0·005	0·0202	0·0190

The observed velocities of reaction are from determinations of Ostwald (at 25° C.); the calculated ones from later determinations of the conductivity of the different acids. The agreement is perfect, and within the errors of observation.

The hydroxyl ions also exert a catalytic influence on many reactions. Thus, for instance, the esters (*e.g.* ethyl acetate) are saponified by the hydroxyl ions according to the equation—



The velocity of this reaction is proportional to the number of  $\bar{\text{OH}}$ -ions present.<sup>1</sup> For the strong bases in 0·025 normal solution Reicher found the following values for the velocity of reaction at 9·4° C.:—

$$\begin{aligned} \text{KOH}, & 2·30; \text{NaOH}, 2·31; \text{Ca(OH)}_2, 2·29; \text{Sr(OH)}_2, 2·20; \\ & \text{Ba(OH)}_2, 2·14; \end{aligned}$$

whereas ammonia gave only 0·011. The strong bases may be regarded as almost completely dissociated into their ions at this high dilution, the mono-acid bases a little more so than the diacid ones. In accordance with this all the strong

<sup>1</sup> Reicher, *Ann. d. Chem. u. Pharm.*, 1885, **228**, 275.

bases give nearly the same constant, the mono-acid showing a little higher value than the diacid ones. The figure 0·011 for ammonia is lower than the theoretical value 0·026, because of the presence of the ammonium ions of the salt formed during the process (cf. p. 180), as I<sup>1</sup> have shown by a closer investigation.

One of the most important applications of the theory of electrolytic dissociation was that by Nernst,<sup>2</sup> for calculating the velocity of diffusion. According to van't Hoff's ideas, diffusion is produced by difference in the osmotic pressure of the ions in solutions of different concentration. Therefore, if we know the friction of the ions during their passage through the surrounding water, it should be possible to calculate the rate of diffusion by means of the known laws of osmotic pressure in salt solutions, as given by van't Hoff's theory and by that of electrolytic dissociation. Now, from electrical measurements of Kohlrausch and others on the conductivity of solutions, we know the velocity with which the ions move under the influence of known electrical forces, and from these experiments Kohlrausch had already calculated the friction of the ions in water at different temperatures.

Nernst had only to divide the osmotic pressure by the sum of the friction of the two ions of the salt in question to get its coefficient of diffusion at extremely great dilutions. Now, the experimental determinations of the coefficient of diffusion do not refer to extremely dilute solutions, so that there is a certain difference between the observed and calculated values, the latter being in general a little higher. For instance, the observed and calculated values are for—

HCl, 2·30 and 2·43; KOH, 1·85 and 2·07; NaCl, 1·08 and 1·17;  
LiCl, 0·97 and 0·99.

The agreement is as good as might be expected, and there is no doubt that Nernst, by the aid of the two theories of modern physical chemistry, has found the correct explanation of the phenomenon of diffusion.

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1887, 1, 110; 1888, 2, 289.

<sup>2</sup> Nernst, *Zeit. physikal. Chem.*, 1888, 2, 613.

There is another phenomenon connected with diffusion, to which I might draw attention in a few words, because it is easily explicable according to the theory of electrolytic dissociation, and seems quite inexplicable without it. If hydrochloric acid is dissolved in water, and pure water is poured above this solution, the solution will soon become charged negatively, and the water above positively, because the  $\text{H}^+$ -ions move about 5 times as quickly (at 12° C.) as the  $\text{Cl}^-$ -ions. The observed diffusion constant of dilute HCl, as also that calculated according to Nernst, is 2.09 at 12° C. If there were no electric charges to exert their influence, the diffusion-constant would be 6.17 for  $\text{H}^+$ -ions. Now, I<sup>1</sup> have found that if a substance such as alcohol or cane-sugar, or even a salt, is dissolved in the water where the diffusion is taking place, the movement of the diffusing molecules is always hindered, so long as they consist of non-electrolytes, *i.e.* when the diffusing molecules are not electrically charged. Therefore, if the molecules of HCl were not dissociated into charged ions, we might expect with certainty that their diffusion would proceed more slowly (about 9 % according to other experiments) in a normal solution of sodium chloride than in pure water.

But just the reverse is the case. The electric charge not only draws back the  $\text{H}^+$ -ions, but also the  $\text{Na}^+$ -ions. The force acting is, so to say, divided between a greater number of molecules, and it is easy to calculate that if for every molecule of HCl there are  $n$  molecules of NaCl, the diffusion constant  $k$  of the  $\text{H}^+$ -ions (we say of the acid) will have the following values (at 12° C.):

$n =$	0	0.1	0.2	0.5	1	2	5	10	$\infty$
$k =$	2.09	2.20	2.30	2.58	2.96	3.52	4.44	5.07	6.17

If the number of NaCl molecules is exceedingly great, the electrical force will exert no sensible influence upon the movement of the  $\text{H}^+$ -ions; the diffusion will go on just as if there were no electrical force to hinder it, and  $k$  will reach the value 6.17. In the experiments, a cylindrical vessel was one-quarter

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1892, **10**, 51.

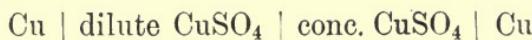
filled with a solution containing 1·04 mole HCl, dissolved in the one case in 0·1 and in the other case in 0·67 molar NaCl. The upper three-quarters were then filled with solutions of the same NaCl content, but free from HCl; the diffusion-constants were observed to be 2·50 and 3·51 respectively, instead of 2·09 for HCl in pure water; the calculated values were 2·43 and 3·47 respectively. In the same way the lower quarter of the vessel was filled with 0·54*n* NaOH, and the diffusion measured, the solvents being pure water, 0·067*n* NaCl, and 0·25*n* NaCl solutions at 12° C. The following diffusion-constants of the base (really of the OH-ion) were found: 1·15, 1·51, and 1·90, whereas the calculated figures were 1·15, 1·50, and 2·00. A great number (twenty-five) of other experiments with different concentrations of hydrochloric or nitric acid, sodium or potassium hydrate, in different salt solutions, were carried out, all with the same result, namely, that the diffusion-constant increased almost in quantitative agreement with the theory, and in the opposite way to that which would have been expected if the diffusing substances had not been electrolytically dissociated.

The study of the electromotive forces existing between electrolytes, by means of the theory of Nernst, which is based upon modern conceptions, has given us the first mechanical representation of the mode in which electromotive forces are produced.

Nernst makes use of the idea of "solution pressure," which is based on the theory of van't Hoff, and is a measure of the tendency of a substance to go into solution, just as the vapour-pressure of a liquid denotes the tendency of the liquid to assume the gaseous state. The power which the Daniell cell has of doing work is then expressed as follows: Zinc has a much greater tendency to go into solution as an ion than copper has. In the Daniell cell, when zinc dissolves, forming ions, and copper is deposited, positive electricity must simultaneously flow through the liquid from the zinc side to the copper side, and in order that no opposing electrostatic charges shall result, it must be conducted back from the copper to the zinc pole by means of a metallic wire. The greater tendency of the zinc to go into solution, compared with that of copper, can consequently be used in the performance of work. The

mechanical analogy is as follows : Two vessels, the one containing ethyl ether and the other water, are connected by means of a cylinder in which is a movable piston. Air and other gases are supposed to be absent. The ether has a greater vapour-pressure than the water, and consequently the piston tends to move from the vessel containing ether towards the one containing water. This tendency can be used to do work, *e.g.* to raise the piston, together with weights placed upon it.

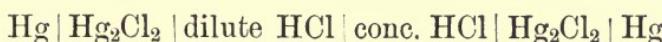
Nernst has deduced the following formula for the electromotive force  $\epsilon$ . In a concentration cell of the first order and with unpolarizable electrodes (see p. 67), as, for instance, the combination<sup>1</sup>—



$$\epsilon = \frac{1.99T \times 10^{-4}}{n} \cdot \frac{2v}{u+v} \cdot \log \frac{p_1}{p_2},$$

where  $p_1$  and  $p_2$  are the concentrations of the dilute and concentrated solutions respectively ;  $u$  is the migration velocity of the anion (see p. 55), and  $v$  that of the cathion ;  $n$  is the valency of the ion which is deposited, and in this case is 2.

For a concentration cell of the second order and with unpolarizable electrodes, *e.g.*—



$$\epsilon = - \frac{1.99T \times 10^{-4}}{n} \cdot \frac{2u}{u+v} \cdot \log \frac{p_1}{p_2}.$$

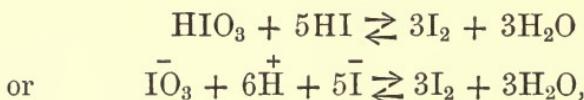
The letters have the same significance as before, and in this case  $n$  is 1.

Measurements of electromotive force thus give us a very valuable method for determining the quantity of one kind of ion in the presence of other ions or molecules ; it is possible to measure ionic concentrations which are extremely small, as, for example, those of the Ag-ions in saturated solutions of AgI and KAg(CN)<sub>2</sub>.

An extremely interesting research, which is based on such

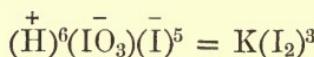
<sup>1</sup> Nernst, *Zeit. physikal. Chem.*, 1889, **4**, 129.

measurements and was carried out by Sammet,<sup>1</sup> may be quoted as an example. Sammet studied the equilibrium represented by the equation—



and also the corresponding equilibrium for bromic and hydrobromic acids. If only a very small quantity of HI is present, the reaction is complete in the direction from left to right. In order to obtain a state of equilibrium, Sammet made use of the slight solubility of silver iodide, so as to have a low concentration of the I-ion. The experiments were carried out either by shaking solid AgI with a solution of HIO<sub>3</sub>, or else by shaking solid AgIO<sub>3</sub> and I<sub>2</sub> with pure water. The solubility of the AgI in the presence of KI, as also that of AgIO<sub>3</sub> in the presence of KIO<sub>3</sub>, was determined by measurements of the electromotive force of concentration cells. The concentration of the I<sub>2</sub> could be varied by adding CCl<sub>4</sub> containing dissolved iodine. The concentrations of the IO<sub>3</sub>-ions and of the H-ions were determined by titration.

It was found, in agreement with theory, that the following equilibrium equation holds:—



The alteration of the constant K with the temperature was determined, and found to be in agreement with the second equation given on p. 148. The constant K was also determined by measurements of electromotive force, and found to be in agreement with theory.

Again, the catalytic processes furnish us with a similar method of determining the concentration of ions, especially the ions  $\overset{+}{\text{H}}$  and  $\bar{\text{OH}}$ , which play the most important rôle in nature.

A reaction which is very sensitive to  $\overset{+}{\text{H}}$ -ions, viz. the

<sup>1</sup> Sammet, *Zeit. physikal. Chem.*, 1905, **53**, 641.

decomposition of ethyl-diazoacetate, has recently been investigated by Bredig and Fraenkel.<sup>1</sup> This reaction will probably be more suitable than any hitherto studied, for measuring small concentrations of the H-ion.

<sup>1</sup> Bredig and Fraenkel, *Z<sup>eit.</sup> für Elektrochem.*, 1905, 11, 525.

## CHAPTER XIV

### *PROBLEMS TO BE SOLVED. OBJECTIONS*

ALREADY in 1890, only three years after the appearance of the fully developed electrolytic dissociation theory, van't Hoff spoke of it as having "become almost a fact."<sup>1</sup> This may be said much more truly to-day, now that it, together with the theory of osmotic pressure, has shown its fruitful applicability in nearly all departments of modern science. Nevertheless, some questions still remain to be solved by means of new investigations and generalizations. The deviation (even in 0·01 normal solution) of the salts and other strongly dissociated electrolytes from the simple law of mass-action, which was found by Ostwald and Bredig to be valid for weak acids and bases, is of the greatest importance.

This deviation, which quite recently has been subjected to a very careful and extended examination by Prof. Jahn<sup>2</sup> in Berlin, recalls the more simple and apparent relations for undissociated substances, *e.g.* for cane-sugar. The depression  $E$  of the freezing-point of solutions of cane-sugar is not proportional to the concentration  $n$  as it should be if van't Hoff's law holds. According to this law,  $E = 1\cdot85n$  if  $n$  is expressed in moles per litre; or  $E = 0\cdot0541n$ , if  $n$  is given as grams of sugar in 100 c.c. Instead of following this law, the depression increases more rapidly, as is seen from the following table, where  $n$  is expressed in grams per 100 c.c. :—

<sup>1</sup> van't Hoff, *Zeit. physikal. Chem.*, 1890, **5**, 322.

<sup>2</sup> Jahn, *Zeit. physikal. Chem.*, 1900, **33**, 545, **35**, 1; 1901, **37**, 490 and 673.

$n$	E	$\frac{E}{n}$	$\rho$	$\frac{\rho}{n}$	$\frac{\rho}{E}$
40	3·41	0·085	11·68	0·292	3·43
20	1·37	0·068	4·54	0·227	3·32
10	0·612	0·061	2·07	0·207	3·38
4	0·228	0·057	0·77	0·192	3·37

This is caused by the deviations from the simple law at higher concentrations. Evidently with decreasing concentration the value  $\frac{E}{n}$  tends to the limit 0·054, as van't Hoff's law demands. Similarly, it is well known that gases do not follow Boyle's law at higher concentrations; the recent work of Lord Rayleigh<sup>1</sup> has shown that Boyle's law is valid at very low pressures, although this was formerly doubtful (Mendeléeff,<sup>2</sup> Bohr<sup>3</sup>). Just as the deviations of gases from the ideal gas laws are explained by the mutual attraction of their molecules, so in the same way the deviation from van't Hoff's law may be understood as being due to the attraction of the dissolved molecules for each other, and especially for the solvent, in this case water. It is not astonishing that the deviations for the dissolved molecules are much greater than for gaseous molecules, in about the same proportion as the liquid is denser than the gas. Hence we may say that these deviations for solutions are in perfect accordance with our experience with gases.

It is interesting to note how the velocity of reaction changes with the concentration. This, according to Ostwald's measurements, is indicated in the table under the heading  $\rho$ , which represents this velocity at 25° C., using 0·5 normal HCl. Evidently  $\rho$  increases with the concentration ( $n$ ), but much more rapidly than this quantity, as the figures under  $\frac{\rho}{n}$  indicate. The startling fact is, that the velocity of reaction  $\rho$  is nearly proportional to the lowering of the freezing-point or to the osmotic

<sup>1</sup> Rayleigh, *Trans. Roy. Soc.*, 1901, **196**, 205; *Proc. Roy. Soc.*, 1905, **74**, 446; *Phil. Trans.*, A, 1905, **204**, 351.

<sup>2</sup> Mendeléeff, *Bull. de l'Ac. de St. Pétersbourg*, 1874, **19**, 469.

<sup>3</sup> Bohr, *Ann. Physik. u. Chem.* (3), 1886, **27**, 459.

pressure of the cane-sugar in the solution, as the figures in the last column show.

The velocity of reaction enters into the equation of equilibrium (cf. p. 140), and therefore it would be more exact to write the two factors of this equation, not as the product of the concentrations of the reacting molecules (or ions), but as the product of their osmotic pressures.

Now, as said above, the most strongly dissociated electrolytes do not follow the law of mass-action, which Ostwald and Bredig have shown to be valid for weak acids and bases. This may easily be understood as a consequence of the deviation of the osmotic pressure from proportionality with the concentration. Consider a solution of a salt in water; the depression of the freezing-point may, if the solution is very weak, be calculated as being proportional to the total number of ions and undissociated molecules. But at higher concentrations deviations occur, just as in the case of cane-sugar, and in most cases the observed freezing-point is lower than the calculated one. As Noyes<sup>1</sup> has recently shown, the difference between the calculated (from the electrical conductivity) and observed values of the lowering of the freezing-point does not exceed more than 2 or 3 %, as long as the concentration of the salts examined (of the type KCl and K<sub>2</sub>SO<sub>4</sub>) is not greater than 0·25 normal. The heat of solution of potassium perchlorate has been calculated with about the same degree of exactitude (within 1·1 %) from the conductivity. This seems to me to indicate that the chief cause of the deviation of the osmotic pressure from proportionality with the concentration is probably the quantitatively unimportant undissociated fraction of the salt.

The molecular lowering of the freezing-point, which, because of the decreasing dissociation, might be expected to decrease with increasing concentration, does not fulfil our expectations, excepting for weak solutions, where the deviations from van't Hoff's law are not so very important. This is due to the excess of the osmotic pressure over the calculated value, which excess increases with concentration. At medium concentrations, therefore, a minimum value of the molecular

<sup>1</sup> Noyes, *Zeit. physikal. Chem.*, 1898, **26**, 699; *Science*, 1904, **20**, 599.

lowering is often found, which thereafter increases with the concentration. This was already shown by my researches in 1888<sup>1</sup> for solutions of  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CuCl}_2$ , and  $\text{CdI}_2$ . An analogous effect is found for the diffusion constant, and is due to the same cause, as I pointed out in 1892 (especially for salts of the type  $\text{NaCl}$ ).<sup>2</sup> The assertion which is made at times that these facts are not in accordance with the prevalent theory, is obviously not well founded.

Even some weak acids do not conform very closely to the law of Ostwald. The majority of these belong to the very important group of so-called *amphoteric* electrolytes, this name being given to them because they are both acids and bases at the same time. The best known are the amido-acids, *e.g.*, aspartic acid, and amidobenzoic acid, which play a highly important rôle in physiological chemistry; the derivatives of albumen also belong to this group. The apparent deviation of these acids from Ostwald's law has been fully explained by the investigations of James Walker<sup>3</sup> and others.

It has often been found that solutions in solvents other than water behave in a rather irregular manner. The most difficult to explain are some results of Kablukoff,<sup>4</sup> Euler,<sup>5</sup> Godlewski,<sup>6</sup> Kahlenberg and Ruhoff,<sup>7</sup> Plotnikoff<sup>8</sup> and especially Lincoln,<sup>9</sup> who have found solutions, in which the molecular conductivity, *i.e.* according to the dissociation theory, the electrolytic dissociation, decreases with increasing dilution. Steele, McIntosh, and Archibald<sup>10</sup> have obtained similar results. They investigated the solutions of organic compounds, such as ether and acetone, in the halogen hydrides, and under certain defined conditions they found an "abnormal" alteration of the

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1888, **2**, 496.

<sup>2</sup> *Ibid.*, 1892, **10**, 88.

<sup>3</sup> J. Walker, *Proc. Roy. Soc.*, 1904, **73**, 155. *Zeit. physikal. Chem.*, 1904, **49**, 82; 1905, **51**, 706.

<sup>4</sup> Kablukoff, *Zeit. physikal. Chem.*, 1889, **4**, 429.

<sup>5</sup> Euler, *Zeit. physikal. Chem.*, 1899, **28**, 619.

<sup>6</sup> Godlewski, *Anz. Ak. Wiss. Krakau*, 1904.

<sup>7</sup> Kahlenberg and Ruhoff, *Journ. physical Chem.*, 1903, **7**, 254.

<sup>8</sup> Plotnikoff, *Zeit. physikal. Chem.*, 1904, **48**, 224.

<sup>9</sup> Lincoln, *Journ. physical Chem.*, 1899, **3**, 457.

<sup>10</sup> Steele, McIntosh and Archibald, *Trans. Roy. Soc. A.*, 1905, **205**, 99.

molecular conductivity with the dilution. The authors show that the abnormal behaviour can be explained by assuming that  $n$  ( $= 2$  or  $3$ ) molecules of the solute form an electrolytically conducting compound with the solvent. The law of mass action demands that the number of molecules which may dissociate, expressed as a fraction of the dissolved molecules, decreases with increasing dilution, and consequently the simultaneous increase in the molecular conductivity can be more than compensated. This method of explanation is applied to other similar measurements (those of Kahlenberg and Ruhoff, and of Plotnikoff), and the necessary calculations made. The investigations cannot, as yet, be considered final, but they nevertheless show that the apparent contradiction is not altogether inexplicable.

The researches of other investigators have led to similar results. An investigation by J. Wallace Walker and F. Godschall Johnson<sup>1</sup> of the conductivities of  $HgCl_2$ ,  $KCl$ ,  $KI$ , and  $KCN$  in acetamide showed that with the last three salts the abnormality exists. An investigation of the migration of the ions appears to indicate that they enter into combination with the solvent.

In some other cases a closer investigation has shown the supposed deviation from theory, found by previous observers, to have no sufficient foundation. Thus, for instance, Wakeman<sup>2</sup> had drawn the conclusion from his measurements that various weak acids, in solutions containing water and ethyl alcohol, do not obey Ostwald's dilution law, which is found to hold good for their aqueous solutions. The recent measurements of Godlewski<sup>3</sup> have shown that Wakeman's measurements are incorrect, and that Ostwald's law is valid in this case also. We thus have grounds for believing that other difficulties will be disposed of on closer investigation.

Although the simple gas laws are not applicable to strongly dissociated electrolytes, except in the case of very (below 0·01 normal) dilute solutions, experiment has furnished us with

<sup>1</sup> Walker and Johnson, *Journ. Chem. Soc.*, 1905, **87**, 1597.

<sup>2</sup> Wakeman, *Zeit. physikal. Chem.*, 1893, **11**, 49.

<sup>3</sup> Godlewski, *Anz. Akad. Wiss. Krakau*, 1904, 239.

some empirical rules, which may be used with success till their theoretical foundations are cleared up.

Such a rule is that of Rudolphi<sup>1</sup> or van't Hoff<sup>2</sup> for calculating the dissociation of strong electrolytes. Van't Hoff replaced the power 2 by the power  $\frac{3}{2}$  in the equation—

$$(\text{Conc. } \text{XA}) = \text{const.} (\text{conc. } \text{X})^{\frac{3}{2}},$$

which is required by the gas laws when there is an equilibrium between the undissociated molecules XA and the ions X and A (present in equal concentrations). He found a fairly good agreement between the equation and the experimental results. This may, for instance, be seen to be the case from the following figures for silver nitrate at 25° C.  $\mu_v$  is the molecular conductivity (equal to the specific conductivity divided by the concentration) at the dilution of  $v$  litres per gram-molecule AgNO<sub>3</sub>,  $\alpha$  is the dissociated fraction (equal to  $\frac{\mu_v}{\mu_\infty}$ ), and K is the value of the constant in the equation  $\frac{1 - \alpha}{v} = K \left( \frac{\alpha}{v} \right)^{\frac{3}{2}}$ .

$v$	$\mu_v$	$\alpha$	K
16	102.3	0.828	1.00
32	108.0	0.875	1.08
64	111.0	0.899	0.96
128	114.3	0.926	1.03
256	116.9	0.947	1.05
512	118.7	0.962	1.07
$\infty$	123.5	1.00	—

The different values of K lie very near to the mean 1.03, showing that the equation holds good.

A still better agreement may evidently be obtained if the power to which the concentration of the ions is raised is determined from the experiments themselves, and not necessarily put equal to 1.5. This was first done by Storch<sup>3</sup>; according

<sup>1</sup> Rudolphi, *Zeit. physikal. Chem.*, 1895, **17**, 385.

<sup>2</sup> van't Hoff, *Zeit. physikal. Chem.*, 1895, **18**, 300.

<sup>3</sup> Storch, *Zeit. physikal. Chem.*, 1896, **19**, 13.

to Noyes,<sup>1</sup> the power in different cases varies between the values 1·43 and 1·56. In this manner it is possible to represent the observed values of the conductivity of salts up to a concentration of 0·2 normal.

It has been found that the equation of van't Hoff with the power 1·5 is valid not only for salts composed of two ions, but also for salts composed of a greater number of ions. On theoretical grounds it seems necessary to assume that it cannot be applicable to extremely dilute solutions, for in this case the law of mass-action must be fulfilled.

Another rule, which has been found to be approximately true, says that salts of the same type are dissociated to nearly the same extent at the same molecular concentration, and that the undissociated fraction remaining at this concentration is proportional to the product of the valencies of the two ions. Thus, for instance, in 0·05 normal solutions of salts of the type KCl (valencies 1 and 1), the undissociated fraction at 18° C. reaches a mean value of 13·5%; in salts of the type CaCl<sub>2</sub> or K<sub>2</sub>SO<sub>4</sub> (valencies 2 and 1 or 1 and 2) it has about double the value, viz. 30%; and for salts of the type CuSO<sub>4</sub> (valencies 2 and 2) it is about 60%. This rule is a modification, made by Noyes,<sup>2</sup> of a statement by Ostwald.<sup>3</sup>

The general laws of equilibrium indicate that if we mix solutions of two weak acids, HA and HA<sub>1</sub>, which contain the same number of ions per cubic centimetre (such solutions are called isohydric), the degree of dissociation does not change. Before mixing, the following equation holds, in accordance with the law of mass action :—

$$(\text{Conc. of HA}) = \text{const.} (\text{conc. of } \overset{+}{\text{H}}) \times (\text{conc. of } \overset{-}{\text{A}}).$$

If the acids are mixed in the proportion of 1 to  $n$ , the term (conc. of HA) is diminished in the proportion 1 to  $(n + 1)$ , the term (conc. of  $\overset{+}{\text{H}}$ ) remains unchanged, and the term (conc. of  $\overset{-}{\text{A}}$ ) is also diminished in the proportion 1 to  $(n + 1)$ . It therefore

<sup>1</sup> Noyes, *Science*, 1904, **20**, 582.

<sup>2</sup> *Ibid.*, 1904, **20**, 584.

<sup>3</sup> Ostwald, *Zeit. physikal. Chem.*, 1887, **1**, 74, 97. Cf. Walden, *Zeit. physikal. Chem.*, 1887, **1**, 529; 1888, **2**, 79; 1891, **8**, 775.

follows that if equilibrium originally existed between the concentrations in the solution of the acid HA, it will also exist after mixing the two solutions. The same is evidently true for the solution of the acid  $\text{HA}_1$ . If we wish, therefore, to calculate the conductivity of a solution of two weak acids dissolved in a certain quantity of water, we have to suppose the water divided into two parts, so that two isohydric solutions are formed. If these have the conductivities  $a$  and  $a_1$ , and the volumes  $v$  and  $v_1$ , then the conductivity  $c$  of the mixture can be calculated from the equation—

$$c(v + v_1) = av + a_1v_1.$$

This law, which was deduced theoretically for electrolytes which obey the simple gas laws,<sup>1</sup> has proved to be valid for the strongly dissociated electrolytes also. Thus, for instance, I found, for two salts of the same type,  $\text{KNO}_3$  and  $\text{KClO}_3$  or  $\text{NaNO}_3$ , which are dissociated to the same degree in equinormal solutions, that the difference  $\Delta$  between the observed and calculated values of the conductivity of their mixtures (in 0·5 normal solution) had the following values (at 18°·5 C.):—

8 c.c. 0·5 normal $\text{KNO}_3$	+ 0·9 c.c. 0·5 normal $\text{KClO}_3$	$\Delta$	= - 0·03 %
8 "	" + 2	"	- 0·22 %
8 "	" + 4	"	- 0·26 %
8 "	" + 8	"	- 0·00 %
4 "	" + 8	"	- 0·06 %
2 "	" + 8	"	- 0·10 %
0·9 "	" + 8	"	+ 0·01 %
8 "	" + 2	"	- 0·00 %
8 "	" + 4	"	- 0·05 %
8 "	" + 8	"	- 0·05 %
4 "	" + 8	"	- 0·30 %
2 "	" + 8	"	- 0·33 %

The differences, even in these rather concentrated solutions, do not very much exceed the experimental errors. Still better is the agreement at lower concentrations.

This rule may be extended to a mixture of any number of solutions of electrolytes, provided that the conditions of

<sup>1</sup> Arrhenius, *Ann. Physik. u. Chem.* (3), 1887, **30**, 51; *Zeit. physikal. Chem.*, 1888, **2**, 284.

equilibrium between the different salts are fulfilled at one and the same time. Hence it has been of great use in calculating the real composition of liquids containing many electrolytes in solution, *e.g.* the waters of the ocean, or the humours of the living body.

In the calculation of the degree of dissociation of an electrolyte we have always assumed that the friction of the moving ions against the surrounding fluid may be regarded as independent of the concentration of the salt. This is doubtless true for dilute solutions, but even in 0·1 normal solutions the correction for the alteration in this friction probably reaches 2 to 3 % in some cases, namely, for solutions with great internal friction, such as sodium sulphate or acetate. The probable increase in this correction is approximately proportional to the concentration. A probable value for this correction may be found by putting it equal to the percentage excess of the internal friction of the solution over that of pure water; or, still better, equal to the corresponding percentage decrease of the diffusion coefficient of a non-electrolyte in the solution. For 0·1 equivalent normal solutions of NaCl, Na<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COONa these values are 0·7, 1·8, and 2·8 % respectively for the internal friction, and 0·8, 1·6, and 2·5 % respectively for the diffusion.<sup>1</sup> Reasoning from the close analogy between the process of diffusion and the conduction of electricity, these two corrections, and, as we know from the experimental evidence in other cases, also that for the internal friction, must be of the same order of magnitude. If such a correction for the conductivity were introduced, the figures for the degree of dissociation of salts giving solutions of great internal friction would increase in a remarkable degree. Since now, in a given group of salts (for instance, of the type KCl) the uncorrected values of the degree of dissociation are the lower the greater the internal friction of the solution of the salt examined, it is to be expected that after the introduction of this correction, these values for different salts would agree much better with each other than they do now in their uncorrected state.

Again, the calculations of the degree of dissociation and of the conductivity of mixtures would probably give still better

<sup>1</sup> Arrhenius, *Zeit. physikal. Chem.*, 1892, **10**, 60.

values after the introduction of this correction than at present. Generally speaking, it seems to me to be of the highest importance that this correction should be introduced before entering into further theoretical investigations of the deviations from the simple gas laws, shown by salts in solution.

According to recent investigations of Walden, the molecular conductivity at very high dilutions of tetraethylammonium iodide, in twenty-six different solvents—all of them organic compounds—is very nearly proportional to the fluidity, *i.e.* inversely proportional to the internal friction. The mean deviation from this rule is only 5 %, if some few solvents, among which are water and glycol, are excepted.<sup>1</sup>

From what has been said on the conductivity of mixtures of salt solutions, it is easily seen that an equation of the form proposed by van't Hoff and Storch cannot be valid for mixtures of different salts,  $XA$ ,  $X_1A_1$ , etc. I have proposed the following form in its place:—

$$(Conc. of undiss. XA) = \frac{\text{const. (conc. of ions } \overset{+}{X} \text{)(conc. of ions } \overset{-}{A})}{\sqrt{(\text{total conc. of the ions } \overset{+}{X} + \overset{+}{X}_1 + \dots + \overset{-}{A} + \overset{-}{A}_1 + \dots)}}$$

As will be seen from these remarks, there remains a very large field for research, in order to obtain data for the completion of our present knowledge. We are not entitled to believe that all questions will be settled by new investigations, for new problems are certain to occur during the attempts to solve the old ones.

<sup>1</sup> P. Walden, *Zeit. physikal. Chem.*, 1906, 55, 207.



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